DOCUMENT RESUME

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IDENTIFIERS Boilers; *Feedwater; *Millwrights; Power Plant Operators

ABSTRACT

This packet of three learning modules on feedwater is one of six such packets developed for apprenticeship training for millwrights. Introductory materials are a complete listing of all available modules and a supplementary reference list. Each module contains some or all of these components: goal, performance indicators, study guide (a check list of steps the student should complete), a vocabulary list, an introduction, information sheets, assignment sheet, job sheet, self-assessment, self-assessment answers, post-assessment, instructor post-assessment answers, and a list of supplementary references. Supplementary reference material may be provided. The three training modules cover feedwater types and equipment, feedwater treatments, and feedwater testing. (YLB)

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APPRENTICESHIP

MILLWRIGHT

RELATED TRAINING MODULES

12.1 - 12.3 FEEDWATER

CE 041002

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APPRENTICESHIP

MILLWRIGHT
RELATED TRAINING MODULES

SAFETY

1.1 General Safety
1.2 Hand Tool Safety
1.3 Power Tool Safety
1.4 Fire Safety
1.5 Hygiene Safety
1.6 Safety and Electricity
1.7 Fire Types and Prevention
1.8 Machine Safeguarding (includes OSHA Handbook)

ELECTRICITY/ELECTRONICS

2.1 Basics of Energy
2.2 Atomic Theory
2.3 Electrical Conduction
2.4 Basics of Direct Current
2.5 Introduction to Circuits
2.6 Reading Scales
2.7 Using a V.O.M.
2.8 OHM'S Law
2.9 Power and Watt's Law
2.10 Kirchoff's Current Law
2.11 Kirchoff's Voltage Law
2.12 Series Resistive Circuits
2.13 Parallel Resistive Circuits
2.14 Series - Parallel Resistive Circuits
2.15 Switches and Relays
2.16 Basics of Alternating Currents
2.17 Magnetism

COMPUTERS

3.1 Digital Language
3.2 Digital Logic
3.3 Computer Overview
3.4 Computer Software

TOOLS

4.1 Boring and Drilling Tools
4.2 Cutting Tools, Files and Abrasives
4.3 Holding and Fastening Tools
4.4 Fastening Devices
4.5 Basic Science - Simple Mechanics
4.6 Fasteners

DRAFTING

5.1 Types of Drawing and Views
5.2 Sketching
5.3 Blueprint Reading/Working Drawings
5.4 Working Drawings for Machines and Welding
5.5 Machine and Welding Symbols
5.6 Blueprint Reading, Drafting: Basic Print Reading
5.7 Blueprint Reading, Drafting: Basic Print Reading
5.8 Blueprint Reading, Drafting: Basic Print Reading
5.9 Blueprint Reading, Drafting: Basic Print Reading
5.10 Blueprint Reading, Drafting: Basic Print Reading
5.11 Blueprint Reading, Drafting: Basic Print Reading
5.12 Blueprint Reading, Drafting: Basic Print Reading
5.13 Blueprint Reading, Drafting: Basic Print Reading
5.14 Drafting, Machine Features
5.15 Drafting, Measurement
5.16 Drafting, Visualization

HUMAN RELATIONS

6.1 Communications Skills
6.2 Feedback
6.3 Individual Strengths
6.4 Interpersonal Conflicts
6.5 Group Problem Solving
6.6 Goal-setting and Decision-making
6.7 Worksite Visits
6.8 Resumes
6.9 Interviews
6.10 Expectation
6.11 Wider Influences and Responsibilities
6.12 Personal Finance

BOILERS

7.1 Boilers - Fire Tube Types
7.2 Boilers - Watertube Types
7.3 Boilers - Construction
7.4 Boilers - Fittings
7.5 Boilers - Operation
7.6 Boilers - Cleaning
7.7 Boilers - Heat Recovery Systems
7.8 Boilers - Instruments and Controls
7.9 Boilers - Piping and Steam Traps

TURBINES

8.1 Steam Turbines - Types
8.2 Steam Turbines - Components
8.3 Steam Turbines - Auxillaries
8.4 Steam Turbines - Operation and Maintenance
8.5 Gas Turbines

PUMPS

9.1 Pumps - Types and Classification
9.2 Pumps - Applications
9.3 Pumps - Construction
9.4 Pumps - Calculating Heat and Flow
9.5 Pumps - Operation
9.6 Pumps - Monitoring and Troubleshooting
9.7 Pumps - Maintenance

COMBUSTION

10.1 Combustion - Process
10.2 Combustion - Types of Fuel
10.3 Combustion - Air and Fuel Gases
10.4 Combustion - Heat Transfer
10.5 Combustion - Wood

GENERATORS

11.1 Generators - Types and Construction
11.2 Generators - Operation

FEEDWATER

12.1 Feedwater - Types and Equipment
12.2 Feedwater - Water Treatments
12.3 Feedwater - Testing

AIR COMPRESSORS

13.1 Air Compressors - Types
13.2 Air Compressors - Operation and Maintenance

STEAM

14.1 Steam - Formation and Evaporation
14.2 Steam - Types
14.3 Steam - Transport
14.4 Steam - Purification

MISCELLANEOUS

15.1 Installation - Foundations
15.2 Installation - Alignment
15.3 Circuit Protection
15.4 Transformers
15.5 Trade Terms

TRADE MATH

16.1 Linear - Measure
16.2 Whole Numbers
16.3 Additional and Subtraction of Common Fraction and Mixed Numbers
16.4 Multiplication and Division of Common Fractions and Whole and Mixed Numbers

16.5 Compound Numbers
16.6 Percent
16.7 Ratio and Proportion
16.8 Perimeters, Areas and Volumes
16.9 Circumference and Wide Area of Circles
16.10 Area of Plane, Figures and Volumes of Solid Figures
16.11 Metrics

HYDRAULICS

17.1 Hydraulics - Lever
17.2 Hydraulics - Transmission of Force
17.3 Hydraulics - Symbols
17.4 Hydraulics - Basic Systems
17.5 Hydraulics - Pumps
17.6 Hydraulics - Pressure Relief Valve
17.7 Hydraulics - Reservoirs
17.8 Hydraulics - Directional Control Valve
17.9 Hydraulics - Cylinders
17.10 Hydraulics - Forces, Area, Pressure
17.11 Hydraulics - Conductors and Connectors
17.12 Hydraulics - Troubleshooting
17.13 Hydraulics - Maintenance

METALLURGY

18.1 Included are ILS packets:
W 3010
W 3011-1
W 3011-2
MS 9001 (1-3-4-8-9-6-7-5-2-9)
MS 9200, 9201

POWER DRIVES

19.1 101. A-B-C-D-E
102. C-D-E
103. B-C-D-E
104. A-C-E-F-G-H-I-J
107. A
108. A

WELDING

20.1 602. A-B-C-D-G-I-L-M
603. A-B-F-G-I
W. 3011-1 refer to Mettallurgy 18.1
WE. MA-18

MILLWRIGHT
SUPPLEMENTARY REFERENCE DIRECTORY

Note: All reference packets are numbered on the upper right-hand corner of the respective cover page.

Supplementary Packet #	Description	Related Training Module	
1.8	Concepts & Techniques of Machine Safeguarding, U.S.D.L., O.S.H.A.	1.8	Machine Safeguarding
12.1	Correspondence Course, Lecture 1, Sec. 2, Steam Generators, Types of Boilers I, S.A.I.T., Calgary, Alberta, Canada	7.1	Boilers, Fire Tube Type
12.2	Correspondence Course, Lecture 2, Sec. 2, Steam Generators, Types of Boikers II, S.A.I.T., Calgary, Alberta, Canada	7.2	Boilers, Water Tube Type
12.3	Correspondence Course, Lecture 2, Sec. 2, Steam Generators, Boiler Construction & Erection, S.A.I.T., Calgary, Alberta, Canada	7.3	Boilers, Construction
12.4	Correspondence Course, Lecture 4, Sec. 2, Steam Generators, Boiler Fittings II, S.A.I.T., Calgary, Alberta, Canada	7.4	Boilers, Fittings
12.4	Correspondence Course, Lecture 4, Sec. 2, Steam Generators, Boiler Fitting I, S.A.I.T., Calgary, Alberta, Canada	7.4	Boilers, Fittings
12.5	Correspondence Course, Lecture 10, Sec. 2, Steam Generation, Boiler Operation, Maintenance, Inspection, S.A.I.T., Calgary, Alberta, Canada	7.5	Boilers, Operation
12.7	Correspondence Course, Lecture 3, Sec. 2, Steam Generation, Boiler Details, S.A.I.T., Calgary, Alberta, Canada	7.7	Boilers Heat Recovery Systems
		PUMPS	
13.1	Correspondence Course, Lecture 9, Sec. 2, Steam Generator, Power Plant Pumps, S.A.I.T., Calgary, Alberta, Canada	9.1	Types & Classifications
13.2		9.2	Applications
13.4		9.4	Calculating Heat & Flow
13.6		9.6	Monitoring & Troubleshooting
13.7		9.7	Maintenance
13.3	Correspondence Course, Lecture 6, Sec. 3, Steam Generators, Pumps, S.A.I.T., Calgary, Alberta, Canada	9.3	Construction
13.5		9.5	Operation

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Supplementary Packet #	Description	Related Training Module
14.3 12.8	Correspondence Course, Lecture 6, Sec. 3, Steam Generators, Steam Generator Controls, S.A.I.T., Calgary, Alberta, Canada	14.3 Steam Transport 7.8 Boilers, Instruments & Controls
14.4	Correspondence Course, Lecture 11, Sec. 2, Steam Generators, Piping II, S.A.I.T., Calgary, Alberta, Canada	14.4 Steam Purification
15.1	Correspondence Course, Lecture 1, Sec. 4, Prime Movers, & Auxiliaries, Steam Turbines, S.A.I.T., Calgary, Alberta, Canada	8.1 Steam Turbines, Types
15.2	Correspondence Course, Lecture 4, Sec. 3, Prime Movers, Steam Turbines I, S.A.I.T., Calgary, Alberta, Canada	8.2 Steam Turbines, Components
15.3	Correspondence Course, Lecture 2, Sec. 4, Prime Movers & Auxiliaries, Steam Turbine Auxiliaries, S.A.I.T., Calgary, Alberta, Canada	8.3 Steam Turbines, Auxiliaries
15.4	Correspondence Course, Lecture 6, Sec. 3, Prime Movers, Steam Turbine Operation & Maintenance, S.A.I.T., Calgary, Alberta, Canada	8.4 Steam Turbines, Operation & Maintenance
15.5	Correspondence Course, Lecture 8, Sec. 3, Prime Movers, Gas Turbines, S.A.I.T., Calgary, Alberta, Canada	8.5 Gas Turbines
16.2	Boilers Fired with Wood & Bark Residues, D.D. Junge, F.R.L., O.S.U., 1975	10.2 Combustion Types of Fuel
16.2	Correspondence Course, Lecture 5, Sec. 2, Steam Generators, Fuel Combustion, S.A.I.T., Calgary, Alberta, Canada	10.2 Combustion Types of Fuel
16.3	Correspondence Course, Lecture 5, Sec. 2, Plant Services, Fuel & Combustion, S.A.I.T., Calgary, Alberta, Canada	10.3 Combustion Air & Fuel Gases
17.1	Correspondence Course, Lecture 12, Sec. 3, Steam Generation, Water Treatment, S.A.I.T., Calgary, Alberta, Canada	12.1 Feedwater, Types & Operation
17.2	Correspondence Course, Lecture 12, Sec. 2, Steam Generation, Water Treatment, S.A.I.T., Calgary, Alberta, Canada	12.2 Feedwater, Water Treatments

Supplementary Packet #	Description	Related Training Module
17.3	Correspondence Course, Lecture 7, Sec. 2, Steam Generators, Boiler Feedwater Treatment, S.A.I.T., Calgary, Alberta, Canada	12.3 Feedwater, Testing
18.1	Correspondence Course, Lecture 2, Sec. 5, Electricity, Direct Current Machines, S.A.I.T., Calgary, Alberta, Canada	11.1 Generators, Types & Construction
18.1 18.2	Correspondence Course, Lecture 4, Sec. 5, Electricity, Alternating Current Generators, S.A.I.T., Calgary, Alberta, Canada	11.1 Generators, Types & Construction 18.2 Generators, Operation
19.1	Correspondence Course, Lecture 5, Sec. 4, Prime Movers & Auxiliaries, Air Compressor I, S.A.I.T., Calgary, Alberta, Canada	13.1 Air Compressors, Types
19.1	Correspondence Course, Lecture 6, Sec. 4, Prime Movers & Auxiliaries, Air Compressors II, S.A.I.T., Calgary, Alberta, Canada	13.1 Air Compressors, Types 13.2 Air Compressors, Operation & Maintenance
20.1	Basic Electronics, Power Transformers, EL-BE-51	15.4 Transformers
21.1	Correspondence Course, Lecture 6, Sec. 5, Electricity, Switchgear & Circuit, Protective Equipment, S.A.I.T., Calgary, Alberta, Canada	15.3 Circuit Protection
22.1	Correspondence Course, Lecture 10, Sec. 3, Prime Movers, Power Plant Erection & Installation, S.A.I.T., Calgary, Alberta, Canada	15.1 Installation Foundations

RECOMMENDATIONS FOR USING TRAINING MODULES

The following pages list modules and their corresponding numbers for this particular apprenticeship trade. As related training classroom hours vary for different reasons throughout the state, we recommend that the individual apprenticeship committees divide the total packets to fit their individual class schedules.

There are over 130 modules available. Apprentices can complete the whole set by the end of their indentured apprenticeships. Some apprentices may already have knowledge and skills that are covered in particular modules. In those cases, perhaps credit could be granted for those subjects, allowing apprentcies to advance to the remaining modules.

We suggest the the apprenticeship instructors assign the modules in numerical order to make this learning tool most effective.

SUPPLEMENTARY INFORMATION

ON CASSETTE TAPES

Tape 1: Fire Tube Boilers - Water Tube Boilers and Boiler Manholes and Safety Precautions

Tape 2: Boiler Fittings, Valves, Injectors, Pumps and Steam Traps

Tape 3: Combustion, Boiler Care and Heat Transfer and Feed Water Types

Tape 4: Boiler Safety and Steam Turbines

NOTE: The above cassette tapes are intended as additional reference material for the respective modules, as indicated, and not designated as a required assignment.

Modules 18.1, 19.1, and 20.1 have been omitted because they contain dated materials.

12.1

FEEDWATER — TYPES AND EQUIPMENT

Goal:

The apprentice will be able to describe feedwater types and equipment.

Performance Indicators:

1. Describe types of water.
2. Describe equipment for clarification.
3. Describe equipment for softening.
4. Describe equipment for thermal treatment.

Study Guide

* Read the goal and performance indicators to find what is to be learned from package.
* Read the vocabulary list to find new words that will be used in package.
* Read the introduction and information sheets.
* Complete the job sheet.
* Complete self-assessment.
* Complete post-assessment.

Vocabulary

* Anion exchanger
* Cation exchanger
* Clarification
* closed feedwater heater
* Coagulants
* Deaerator
* Demineralization
* Dissolved gases
* Embrittlement
* Estuarine water
* Filters
* Flash evaporator
* Hard water
* Open feedwater heater
* Rain water
* Scheens and strainers
* Settling basin
* Shell and tube evaporator
* Soft water
* Softening
* Suspended matter

Introduction

Raw water is found in many forms of purity. Rain water hits the earth in a reasonably pure form except for the oxygen and carbon dioxide it has picked up on its way down. In areas with acid rain, it might collect far more than oxygen and carbon dioxide.

Once the water has percolated through earth and rocks, it becomes either hard water or soft water. This depends on the chemicals picked up as it percolated through the rocks.

One can safely assume that all types of water needs treatment before it is placed in a boiler. Such treatments require equipment for clarification, softening and heating. This package describes some of the equipment needed for feedwater treatment.

Information

TYPES OF WATER

Feedwater comes from several natural sources that have different levels of water quality. The basic categories of natural water are:

1. Rain water
2. Hard water
3. Soft water
4. Estuarine water

Rain Water

Rain water has a high level of carbon dioxide and oxygen. This causes it to be corrosive. It is low in mineral content which reduces the problem from scale. Still it must be treated to remove the dissolved gases which cause corrosion.

Hard Water

Hard water is merely rain water that has traveled through rocks and earth. It picks up calcium and magnesium in the process of moving through the earth. The calcium and magnesium is in the form of carbonates, chlorides and sulphates. These compounds become a problem in feedwater in the form of scale. Hard water must be treated before use as feedwater.

Soft Water

Soft water is rain water that moved through insoluble rocks. The water failed to pick up calcium and magnesium. Soft water may contain suspended matter such as leaves, silt and clay particles that were picked up on its trip through the rocks. Soft water must be treated in settling tanks to remove the suspended matter.

Estuarine Water

Estuarine water comes from estuaries of the sea. It is diluted sea water. The closer it is located to the sea, the heavier the chemical concentration will be. Estuarine water requires careful treatment to be made suitable for boiler feedwater.

Information

EQUIPMENT FOR TREATING WATER

Equipment for Clarification

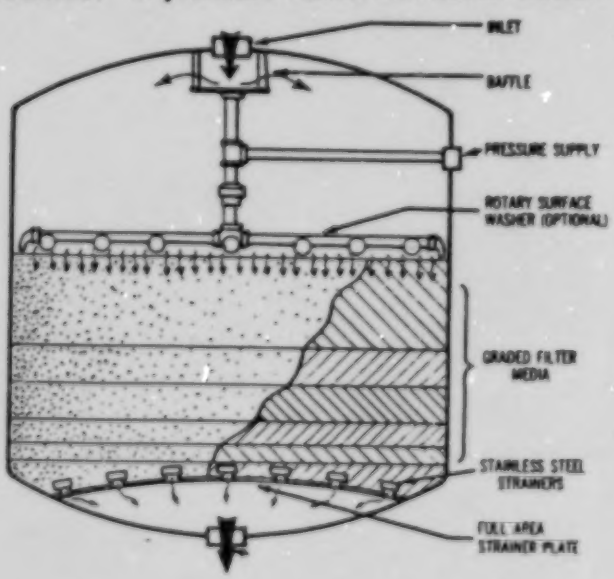
Suspended matter must be removed from feedwater by a process called clarification. This means that the process makes the water clear by removing suspended matter. The equipment uses mechanical treatments to remove particles from the water. The common pieces of equipment for clarification are:

1. Screens and strainers for removing large particles of suspended matter.

2. Settling basins which allows suspended particles to settle to the bottom and be drawn off.

3. Coagulants are sometimes needed to increase the particle size of suspended solids. The particles will then settle to the bottom to be drawn off. This is a mechanical (settling) process even though a chemical coagulant was used to promote settling of the particles.

4. Filters consist of a bed of porous material through which water can pass by either gravity flow or under pressure. The porous material is often sand or anthracite. A pressure filter is shown below.



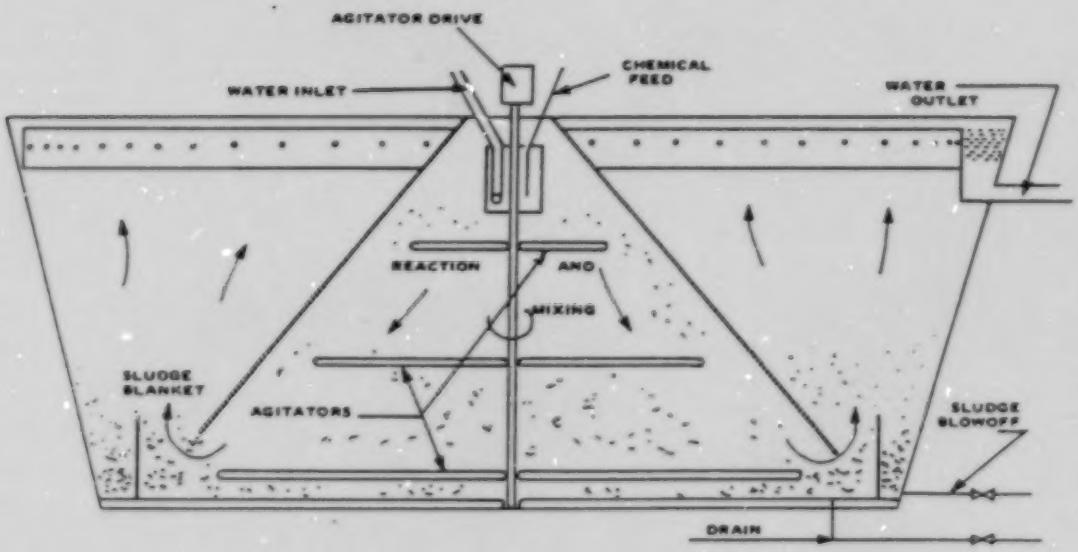
Information

Equipment for Softening

Removal of calcium and magnesium salts from water is often accomplished through softening processess. The common softening processes are:

1. Cold lime-soda
2. Hot line-soda
3. Sodium zeolite
4. Hydrogen zeolite
5. Demineralizion

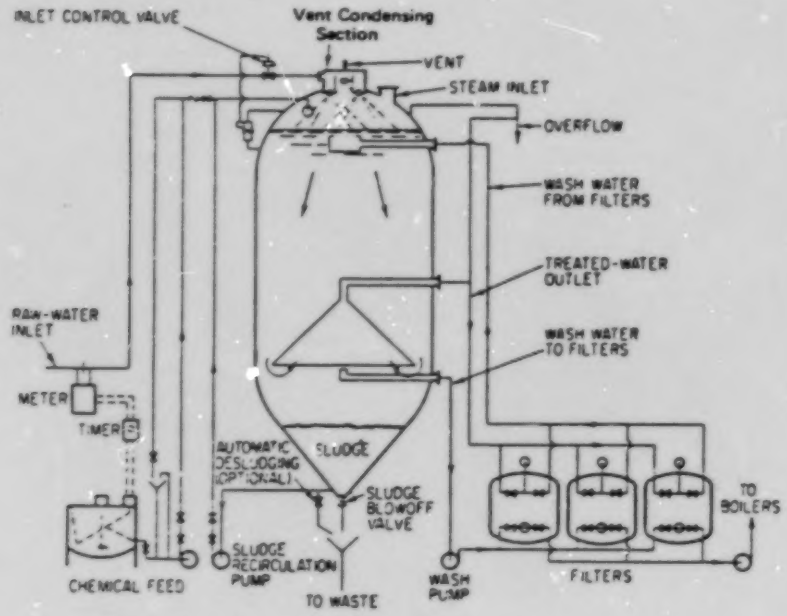
The equipment for cold lime-soda softening requires an agitator to mix the chemicals and a coagulant. The softener combines with scale to form a sludge which can be discharged. The coagulant aids in sludge formation.



Cold Lime-Soda Softener

Information

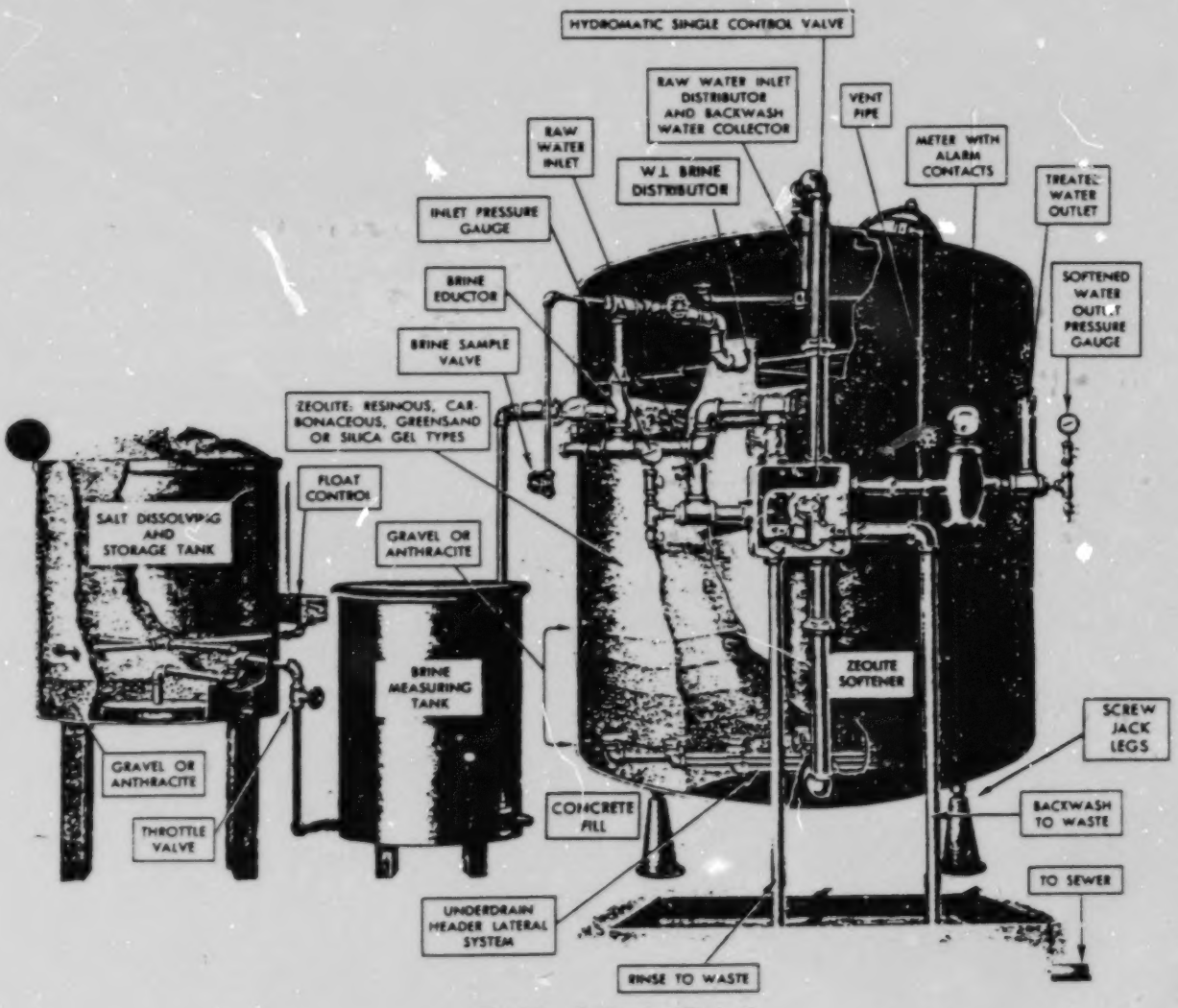
Hot lime-soda requires that the water be heated above 100 C. This causes a quick chemical reaction between the softener and solids in the water. A hot lime-soda softener is pictured below.



Hot Lime-Soda Softener

The sodium zeolite softener exchanges ions with scale forming solids. The scale forming salts are replaced with sodium cations that do not form scale. Some common zeolites are synthetic gel, sulfonated coal and styrene resin. After the zeolite has collected a load of calcium and magnesium cations from the solids, the zeolite container is filled with brine. The brine removes the load of calcium and magnesium ions from the zeolite. The brine can then be flushed out and the zeolite reused. A zeolite softener is shown in detail on the next page.

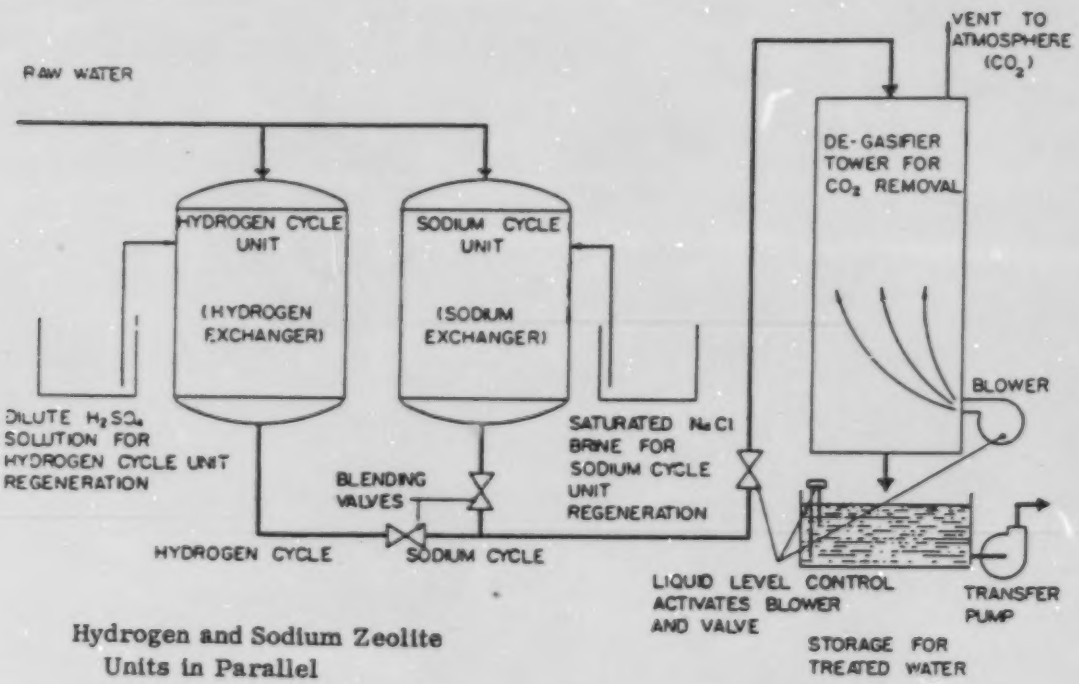
Information



Zeolite Softener Details

Information

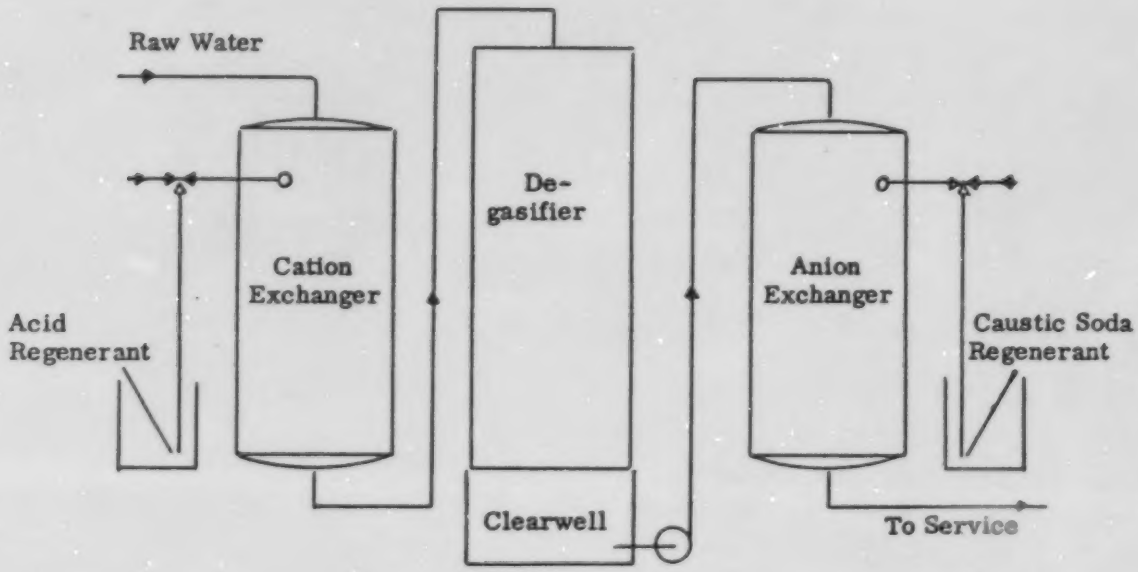
Hydrogen zeolites are often used instead of sodium zeolites. A problem of caustic embrittlement can result from the use of sodium zeolites. Sodium hydroxide was one of the by-products of sodium zeolite softening. This by-product can cause embrittlement. Hydrogen zeolites will remove the scale forming salts without forming the by-products that cause embrittlement. A hydrogen zeolite is made from lignite, sulphonated coal or synthetic resin. A method of carbon dioxide removal must be used with this type of softener. The hydrogen zeolite is often used in parallel with the sodium zeolite unit and a degasifier.



Hydrogen and Sodium Zeolite Units in Parallel

Demineralization uses the principles of anion and cation exchange to remove all salts from the water. A hydrogen zeolite cation exchanger removes sodium, magnesium and calcium. The anion exchanger removes sulphide, chloride and silicia anions. A degasifier removes the carbon dioxide from the water.

Information



Demineralizing Arrangement

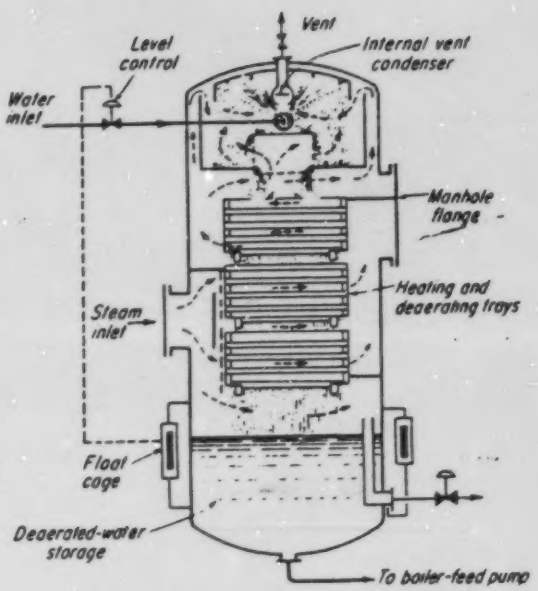
Equipment for Thermal Treatments

Heat can be used to treat feedwater. The most economical use of heat is to remove dissolved gases from the feedwater. Thermal treatment involves the use of:

1. Deaerators
2. Feedwater heaters
3. Evaporators

Dearators are of a spray type or a tray type. Basically, the deaerator heats the water to boiling and removes the gases through a scrubbing process. A combination spray and tray type deaerator is shown.

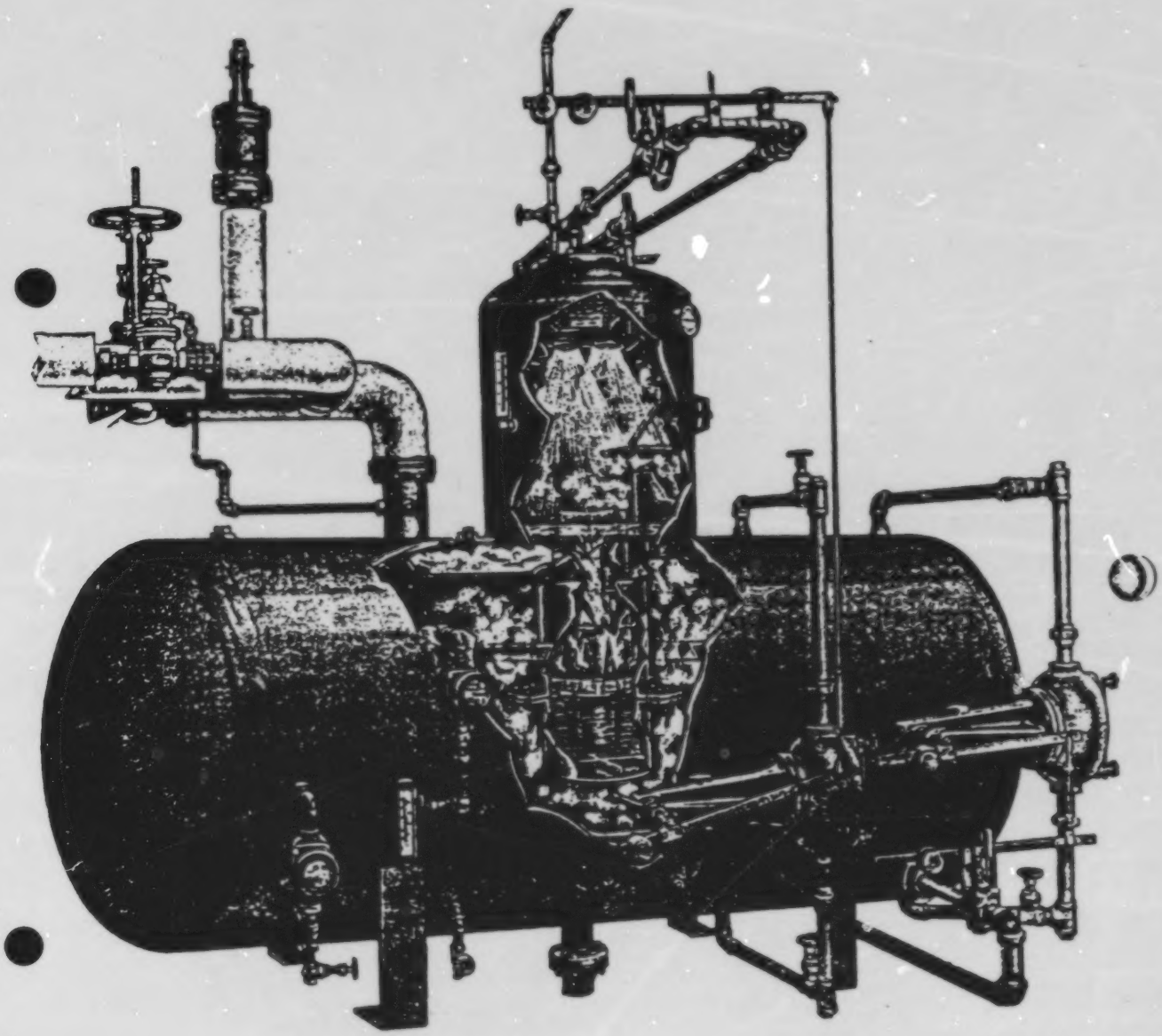
Information



Combination Spray
and
Tray Deaerator

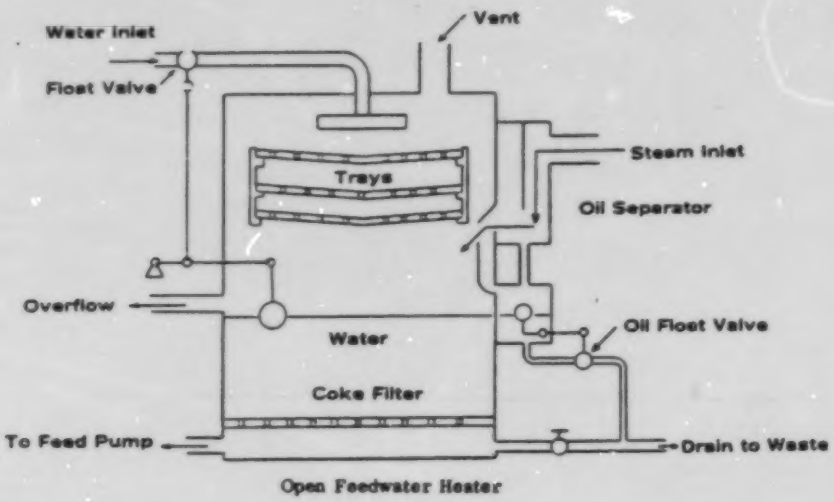
Information

A spray deaerator is pictured below.



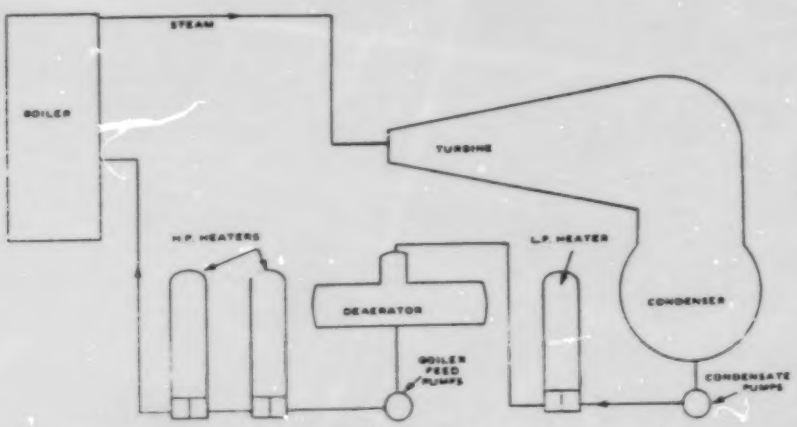
Information

Feedwater heaters are used to soften, deaerate and filter water. They also serve the purpose of heating the feedwater. Bicarbonates are broken into carbon dioxide which has the effect of softening the water. Feedwater heaters may be open or closed types. Open feedwater heaters operate at atmospheric pressure and below boiling point. A closed heater allows water to be heated to high temperatures. The open heater is shown below.



Open Feedwater Heater

A closed feedwater is built into the system as shown.



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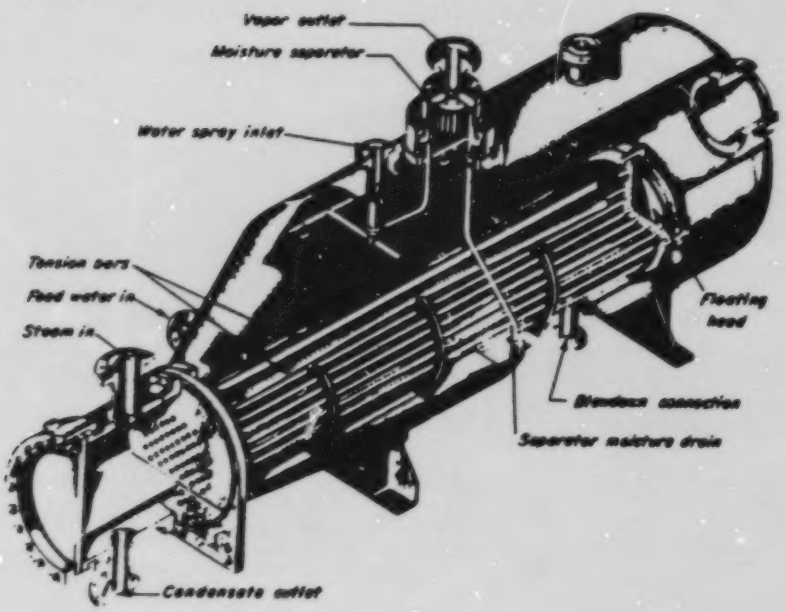
Information

Evaporators are used to distill water for a system. The evaporator removes all solids. A deaerator should be used in tandem with an evaporator to remove the soluble gases. Evaporators are made in three types:

1. Shell and tube
2. Flash
3. Demineralizers

The figure below shows a shell and tube type evaporator.



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Assignment

* Read pages 7 - 33 in supplementary reference.
* Complete the job sheet.
* Complete self-assessment and check answers.
* Complete post-assessment and ask the instructor to check your answers.

Job Sheet

ANALYZE WATER TREATMENT EQUIPMENT AT YOUR JOB SITE OR OTHER VISITATION SITE

* Obtain manufacturer's specifications and instructions for water treatment equipment at a specific site.

* What type of equipment is used for:

  - Clarification?
  - Softening?
  - Thermal treatment?

* What kind of water is used for feedwater?

  - Rain water
  - Hard water
  - Soft water
  - Estuarine water

* Is the equipment appropriate to the needs?

  - What are the water problems?
  - How well are problems controlled?

* Visually inspect water treatment equipment for better understanding of its components.

Self Assessment

Match the following terms with appropriate phrases.

____	1. Settling basin	A. Used to increase the size of particles of suspended matter.
____	2. Cold lime-soda	B. Softener that exchanges ions with scale forming solids.
____	3. Hard water	C. Is actually diluted seawater.
____	4. Sodium zeolite	D. Process for removal of suspended matter from feedwater.
____	5. Soft water	E. Contains scale forming carbonates chlorides and sulphates.
____	6. Rain water	F. Porous bed of anthracite or sand.
____	7. Coagulant	G. Must be treated to remove oxygen and carbon dioxide.
____	8. Clarification	H. May contain suspended matter but is low in solids.
____	9. Filter	I. Allows suspended particles to be drawn off at the bottom.
____	10. Estuarine water	J. Softener that combines with scale to form a sludge.

Self Assessment Answers

I 1.

J 2.

E 3.

B 4.

H 5.

G 6.

A 7.

D 8.

F 9.

C 10.

Post Assessment

Match the following terms and descriptive phrases.

_____ 1.	Hot lime-soda softener	A. Removes carbon dioxide from water.
_____ 2.	Sodium zeolites	B. A common sodium zeolite.
_____ 3.	Hydrogen zeolite	C. Very quick reaction between softener and solids.
_____ 4.	Degasifier	D. A common hydrogen zeolite.
_____ 5.	Demineralization	E. Can cause embrittlement.
_____ 6.	Deaerator	F. Used to avoid embrittlement problems.
_____ 7.	Styrene resin	G. May be shell or tube or flash types.
_____ 8.	Lignite	H. May be of spray or tray types.
_____ 9.	Evaporator	I. May be of open or closed types.
_____ 10.	Feedwater heater	J. Removes all salts from water and uses both anion and cation exchange principles.

Instructor Post Assessment Answers

C 1.

E 2.

F 3.

A 4.

J 5.

H 6.

B 7.

D 8.

G 9.

I 10.

Supplementary References

* Correspondence Course. Lecture 12, Section 3, Third Class. Steam Generation. Southern Alberta Institute of Technology. Calgary, Alberta, Canada.

SOUTHERN ALBERTA INSTITUTE OF TECHNOLOGY
CALGARY, ALBERTA

Correspondence Courses
Power Engineering

SECTION 3

STEAM GENERATION

Third Class
Lecture 12

WATER TREATMENT

THE NEED FOR WATER TREATMENT

If water were H_2O and nothing else, or if all waters carried the same impurities, the treatment of water would be simple and uniform methods could be used. However, pure water never occurs in nature and impurities vary considerably. The closest natural approach to "pure" water is rain, but even rain contains dissolved oxygen and carbon dioxide which has been picked up from the air. Impurities in natural waters depend largely on the source. Wells and springs are classed as ground waters; rivers and lakes as surface waters.

Ground water picks up impurities as it seeps through rock and soil, dissolving some part of almost everything it contacts and therefore groundwater usually contains a considerable amount of dissolved solids. The natural filtering effect of rock and sand usually keep groundwater free and clear of suspended matter. Surface waters often contain suspended matter such as leafmold, sand, silt, sewage and industrial waste. The amount and location of rainfall may rapidly change the amount and type of suspended matter. In addition, surface waters often contain various amounts of dissolved solids as well.

Water which contains large amounts of dissolved solids is termed to be "hard water", while water which contains small amounts of dissolved solids is termed to be "soft water".

If water, which contains impurities, is boiled and changed into steam, impurities are left behind and will form sludge or scale unless they are removed before or during boiling. The more impurities there are in the water and the more water is boiled, the more impurities are left behind to form sludge and scale. Pressure plays another important role. As boiler pressures get higher, boiler water temperatures increase (see steam tables). Higher temperatures produce faster chemical reaction rates so that scale is formed more rapidly and this scale will bake on the metal surfaces more quickly. Not only does this scale cause loss of efficiency, as it transmits heat badly, but it can also be exceedingly dangerous

if it is neglected. With scale, the tubes and plates become cut off from contact with the water in the boiler and the surfaces, no longer cooled by the water, are overheated and the strength of the metal is diminished. In the history of steam engineering, numerous instances occur of boilers having failed, more or less violently, from this cause. Sooner or later, tubes and plates will be overheated so that they no longer withstand the pressure of the steam or the water contained by them. Then a disastrous explosion may occur.

Mud is another form of deposit which sometimes can be nearly as troublesome as scale. Certain chemicals introduced into the boiler to prevent scale will offer an unwelcome compensation by producing mud or sludge instead. Where the circulation inside the boiler is imperfect, this mud accumulates in the more sluggish parts, producing similar problems as scale and causing circulation to some tubes to cease altogether. In order to prevent the formation of mud or sludge, adequate blowdown must always form part of a program which introduces chemicals into the boiler to prevent scale.

In addition to causing deposits, impurities in the feedwater may also cause corrosion, carryover or caustic embrittlement.

Corrosion is the rusting or eating away of metal generally caused by dissolved oxygen or carbon dioxide in the water or a low pH or a combination of all three. Corrosion is one of the most undesirable features in boiler plant operation because it attacks the boiler metal and its harmful effects cannot be repaired without complete renewal. Scale can be removed and carryover stopped, but corrosion damage that has occurred cannot be repaired.

Carryover is a term applied to entrained moisture and associated solids passing from a boiler with the steam. Aside from erratic superheat and mechanical troubles with engines and turbines caused by slugs of moisture, carryover deposits solids in superheaters and on turbine blades. High concentration of dissolved solids in the boiler feedwater greatly increases the tendency for carryover.

Caustic embrittlement is a form of metal cracking which can cause a serious boiler failure. The term "caustic embrittlement" derives its origin from the fact that failure occurs in the presence of a highly concentrated caustic solution and the metal itself fails in a sudden or brittle manner with no apparent deformation of the metal prior to actual failure. To produce caustic embrittlement in boiler metal, three factors are required:

1) a leak and subsequent concentration of boiler water at the point of leakage,

2) a high pH which causes concentrated caustic solution at the leak to attack the metal,

3) a high metal stress in the area of concentration and attack.

The most common areas of embrittlement attack are in rivets and riveted joints in older boilers, tube connections to drums or headers where the tubes have been rolled and stressed and in tube sheets between closely spaced tubes where the tube sheets are heavily stressed. Alternate expansion and contraction of the metal as a result of temperature changes in the boiler can provide small crevices through which boiler water can escape and cause the high caustic concentrations and embrittlement. The power plant engineer has little control over the factors of leakage and stress. The factor which can best be controlled is the pH. If the pH is low enough the water becomes non-embrittling and leakage or stress will not cause embrittlement. At the same time, however, the pH must be high enough to prevent corrosion and scale formation. The exact control of boiler water pH is therefore ext remely important.

Briefly stated, the need and extent of water treatment depends on three main factors:

1) the concentration and type of impurities present in the feedwater,

2) the rate or output of the boiler; the need increasing with higher boiler outputs,

3) the pressure and consequently temperature at which the boiler operates; the need for purer water increasing with higher boiler pressures.

The table following gives an indication of the maximum limits for solids allowed in boiler water. The feedwater total solids is an approximate indication as it depends on many other factors such as percent make-up, type of solids, boiler output, etc.

Operating Pressure (kPa)	Boiler Water Total Solids (ppm)	Feedwater Total Solids (ppm)
0-2000	3500	100
2000-3000	3000	30
3000-4000	2500	20
4000-5000	2000	10
5000-6000	1500	5
6000-7000	1250	4
7000-10000	1000	3
10000-14000	750	2
14000 and higher	500	1

Table 1

FEEDWATER CHEMISTRY

Chemical Formulae

As explained in Lecture 5, Section 2, "Combustion", certain symbols are used to denote both elements and compounds. For example, water is denoted by the symbol H_2O, carbon dioxide by the symbol CO_2, sulphur by the symbol S, and so on. These symbols are actually the chemical formulae for these various substances and indicate what each substance is made up of. In the majority of the methods used for treating feedwater, the impurities are removed by means of chemical reactions. In order to understand how these reactions take place, the chemical formulae for both the impurities and the treatment materials must be known. The following list gives the chemical formulae for the more common compounds associated with water treatment.

Compound	Formula
Aluminum sulphate	$Al_2(SO_4)_3$
Aluminum hydroxide	$Al(OH)_3$
Ammonium hydroxide	NH_4OH
Calcium bicarbonate	$Ca(HCO_3)_2$
Calcium carbonate	$CaCO_3$
Calcium chloride	$CaCl_2$
Calcium hydroxide (hydrated lime)	$Ca(OH)_2$
Calcium sulphate	$CaSO_4$

Carbon dioxide	CO_2
Carbonic acid	H_2CO_3
Hydrazine	N_2H_4
Hydrochloric acid	HCl
Hydrogen zeolite	H_2Z
Magnesium bicarbonate	$Mg(HCO_3)_2$
Magnesium carbonate	$MgCO_3$
Magnesium chloride	$MgCl_2$
Magnesium hydroxide	$Mg(OH)_2$
Magnesium sulphate	$MgSO_4$
Nitric acid	HNO_3
Silicic acid	H_2SiO_3
Sodium aluminate	$Na_2Al_2O_4$
Sodium bicarbonate	$NaHCO_3$
Sodium carbonate (soda ash)	Na_2CO_3
Sodium chloride	Na Cl
Sodium hydroxide (caustic soda)	NaOH
Sodium nitrate	$NaNO_3$
Metasodium phosphate	$NaPO_3$
Monosodium phosphate	NaH_2PO_4
Disodium phosphate	Na_2HPO_4
Trisodium phosphate	Na_3PO_4
Sodium sulphate	Na_2SO_4
Sodium sulphite	Na_2SO_3
Sodium zeolite	Na_2Z
Sulphuric acid	H_2SO_4

Acids, Bases and Salts

Three types of chemical compounds which are of great importance in regard to water treatment are acids, bases and salts. When these are in solution they disassociate into particles which have a definite electrical charge and which are known as ions.

Acids produce an excess of hydrogen ions having a positive electrical charge and which are denoted by H^+. It is this excess of H^+ ions which gives the solution its acidity. Examples of acids are hydrochloric acid HCl, nitric acid HNO_3, and sulphuric acid H_2SO_4.

Bases, also called alkalies, produce an excess of hydroxyl ions having a negative electrical charge and which are denoted by OH^-. It is this excess of OH^- ions which gives the solution its alkalinity. Examples of bases are calcium hydroxide $Ca(OH)_2$, ammonium hydroxide NH_4OH, and sodium hydroxide NaOH.

When an acid is neutralized by a base the result is the formation of a salt. For example, the salt sodium sulphate Na_2SO_4 is formed when sulphuric acid H_2SO_4 is neutralized by the base sodium hydroxide NaOH. In equation form the reaction is:

$$2\ NaOH + H_2SO_4 \longrightarrow Na_2SO_4 + 2\ H_2O$$

Other examples of salts are sodium chloride NaCl, calcium sulphate $CaSO_4$, magnesium carbonate $MgCO_3$, etc.

When a salt is in a solution it will disassociate into positively and negatively charged ions. The positive ions are called cations and the negatively charged ions are called anions.

Thus the salt Na_2SO_4 will disassociate into Na^+ cations and SO_4^- anions.

pH Values

In order to indicate whether a solution is acid or alkaline, a scale of numbers from 0 to 14 is used. These numbers simply indicate the concentration of the H^+ ions and the OH^- ions in the solution. If the concentration of the H^+ ions is equal to the concentration of the OH^- ions then the solution is neutral (neither acidic or alkaline) and the pH value is 7. If the concentration of H^+ ions is greater than that of the OH^- ions then the solution is acidic and has a pH value of below 7. If the concentration of H^+ ions is less than that of the OH^- ions then the solution is alkaline and has a pH value of greater than 7.

The more acidic the solution is the smaller will be the pH value. For example, a pH of 5 will mean the solution is 10 times as acidic as a solution having a pH of 6. A solution having a pH of 4 will be 100 times as acidic as the pH 6 solution.

Similarly, the more alkaline the solution is the greater will be the pH value. A pH value of 9 indicates 10 times the alkalinity of pH 8. A pH value of 10 indicates 100 times the alkalinity of pH 8 and so on.

Table 2 below lists the scale of pH values.

Solution	pH Value
Most acidic	0
	1
	2
Acidity decreases with increasing pH	3
	4
	5
Least acidic	6
Neutral	7
Least alkaline	8
	9
	10
Alkalinity increases with increasing pH	11
	12
	13
Most alkaline	14

pH Scale

Table 2

EXTERNAL WATER TREATMENT

External water treatment refers to the treating of the water before it enters the boiler. It may also be called "feedwater treatment" as it is treatment of water which feeds the boiler. If during the treatment the hardness of the water is reduced, it may be referred to as "water softening".

The chart on Page 8 shows a breakdown of the more common methods of external water treatment. Generally mechanical methods are used to take suspended matter out of the water or clarify the water, chemical methods are used to soften the water and thermal methods are used to take oxygen and other gases out of the water. In some cases one piece of equipment may combine two or more methods while in other cases one method may clarify, soften and degasify the water in one operation.

EXTERNAL WATER TREATMENT CHART			
Method	Equipment	Purpose	Effluent Purity Level (ppm as $CaCO_3$)
Mechanical	Screens and Strainers	Clarify	----
	Settling Basins	Clarify	----
	Coagulators	Clarify	----
	Filters	Clarify	----
Chemical	Cold Lime Soda	Soften	50
	Hot Lime Soda	Soften and Degasify	25-30
	Sodium Zeolite	Soften	1-2
	Hydrogen Zeolite	Soften	0.1-1
	Demineralizer	Soften	0-0.1
Thermal	Deaerator	Degasify and Heating	----
	Open Feedwater Heater	Clarify, Degasify and Heating	----
	Closed Feedwater Heater	Heating and Soften	----
	Evaporators	Soften and Heating	0-1

Mechanical Methods

Insoluble impurities, entering a boiler with the feedwater, tend to stick to hot boiler tubes like dust on flypaper. Practically all surface waters (rivers, lakes, ponds, etc.) contain some amount of mud, silt, clay, decayed vegetation, micro-organisms, sewage and industrial wastes. These insolubles must be removed to prevent fouling of feedwater softeners or to prevent deposits in the boiler.

(PE3-3-12-8)

The insolubles suspended in natural water have a wide range of particle sizes. They may vary from relatively large sand particles to particles which can't be seen (individually) with the naked eye. The larger particles are called sediment. They tend to settle out or can be filtered out. Colloidal particles, however, will stay suspended indefinitely and are small enough to pass through the pores of conventional filters. Collectively the suspended particles are termed turbidity. Clarification for removing turbidity from water may involve the use of screens, settling, chemical coagulation and filtration. If the suspended solids are small (colloidal) chemical coagulation is needed for effective clarification.

1) Screens and Strainers

The purpose of screens and strainers is to prevent the large or free floating particles from entering and damaging or clogging the feedwater supply equipment. They may simply consist of log booms to keep free floating debris away or they may consist of metal screens or strainers of various shapes and coarseness designed to eliminate these particles.

2) Settling Basins

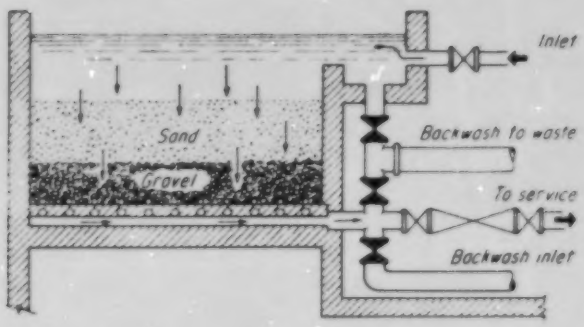
Settling (also called subsidence) may be accomplished by using a simple tank which is filled with the turbid water and allowed to stand. After the sediment has settled, the clarified water is drawn off the top and the settled solids removed from the bottom. The tank is then ready for another cycle. This is the intermittent type of settling basin. Continuous methods of subsidence are more frequently used. This is accomplished by passing water through a basin or tank of such design that the velocity of the water is reduced to a point sufficiently low to permit subsidence. Clarified water is drawn from the tank continuously from an overflow, the settled solids remaining in the bottom of the tank from where they may be removed continuously by mechanically operated rakes or scrapers or periodically by flushing with high pressure jets.

Waters containing turbidity due to relatively large particles or high density solids may be clarified to a substantial degree by settling. It is an economical method of obtaining clarification where it is applicable and in such cases it is often employed prior to coagulation.

After a filter has been in service for a period of time, the filter bed will become plugged with suspended matter removed from the water. When this occurs the filter must be backwashed. Backwashing consists of reversing the direction of flow through the filter thus freeing the trapped material from the bed and washing it to waste.

Gravity Filters

Fig. 2 illustrates a gravity filter which uses a bed of sand supported on a bed of gravel.



Gravity Filter

Fig. 2

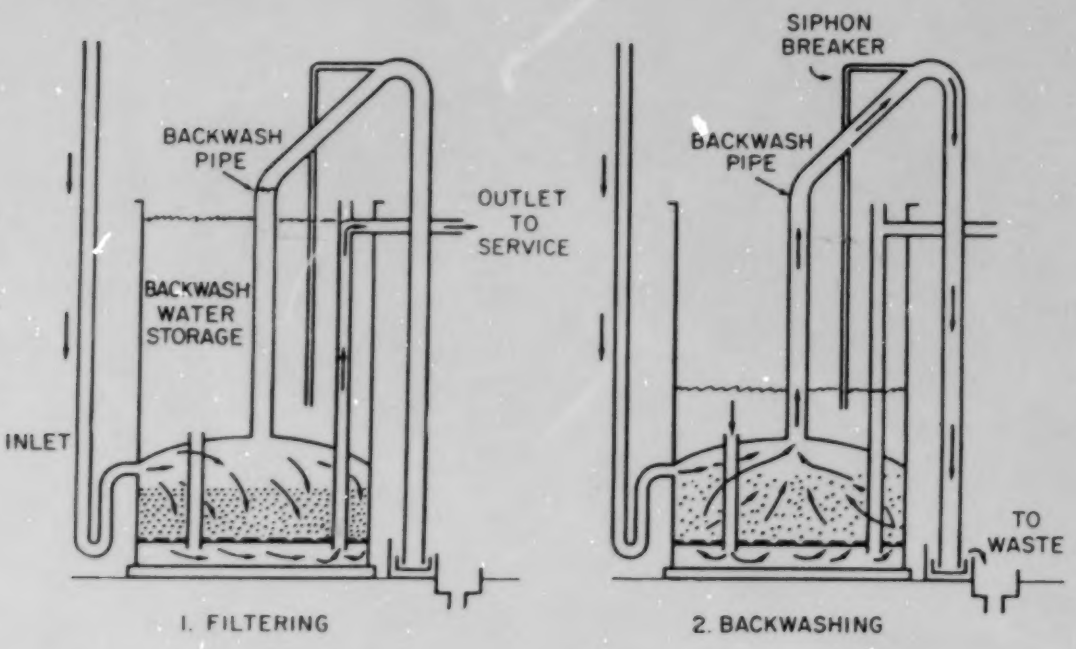
This unit features a rectangular reinforced concrete construction for the filter shell although in some designs the shell is of wood or steel and may be circular in shape. The bed of sand is usually 0.4 m to 0.8 m in depth and the gravel bed between 0.3 and 0.6 m.

The water enters at the top and flows downwardly through the filter bed to the outlet at the bottom. When backwashing is necessary, the flow is reversed with the backwash water entering at the bottom and being discharged at the top to waste.

The filter shown in Fig. 3 is designed to automatically backwash itself when the filter bed becomes sufficiently plugged with dirt.

In this unit the inlet water normally passes downwardly through the filter bed and up the outlet pipe. As impurities accumulate in the filter bed, the level of water in the backwash pipe rises until it finally flows over the loop at the top. The backwash pipe then begins to siphon the water from the space above the bed. This

caused the backwash storage water to flow from the storage space through a pipe to the underside of the bed. It then passes upwardly through the bed to waste thus backwashing the bed. When the storage water level drops below the end of the siphon breaker pipe, the backwashing will stop and normal flow through the filter bed will resume, first filling the backwash storage space and then passing through the outlet to service. The filling of the backwash storage space provides a rinsing period before the filter returns to service.



Automatic Backwashing Gravity Filter

Fig. 3

Pressure Filters

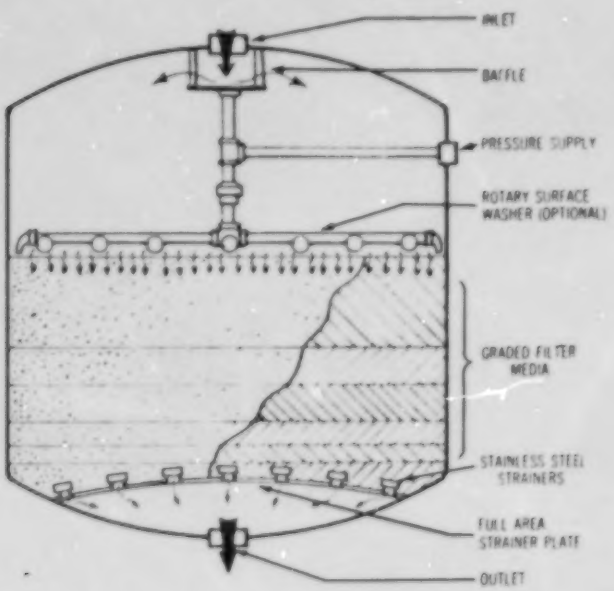
A pressure filter is illustrated in Fig. 4. The shell is of steel and contains a bed of anthracite which is supported on a strainer plate. The water to be filtered is pumped under pressure through the filter, entering at the top and passing down through the filter bed and through stainless steel strainers to the outlet at the bottom.

(PE3-3-12-13)

Pressure gages, not shown in the figure, are installed on the inlet and outlet lines and when the pressure difference between them reaches a certain value, usually from 35 to 55 kPa, it means that backwashing is required.

During the backwashing period, a rotary surface washer may be used to loosen material from the surface of the bed. The water leaves the nozzles of the rotary washer at high velocity which causes the washer arm to revolve.

Frequently, filters are used in conjunction with settling tanks and coagulation. The sequence is to coagulate and settle the impurities in a settling tank and then pass the water through filters for final clarification.



Pressure Filter

Fig. 4

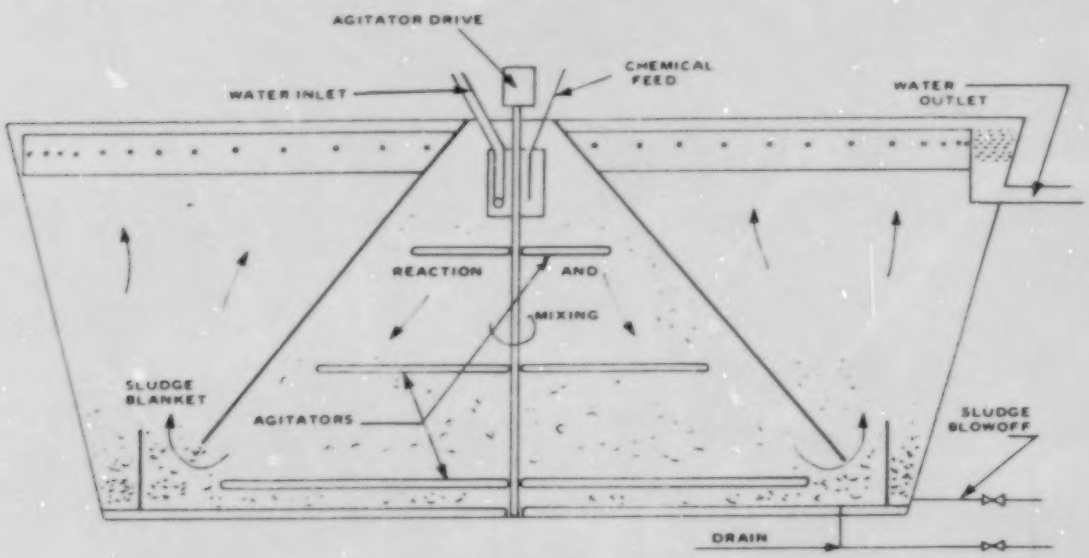
If filters are used alone then a coagulant is usually fed to the filter in order that the finer impurities are formed into larger particles that can be trapped by the filter bed.

Chemical Methods

In the chemical methods of water treatment chemicals are used in one way or another to react with the dissolved solids of the water. This reaction will soften the water by changing the dissolved solids to a highly soluble dissolved solid which does not easily form scale, or by making the dissolved solids insoluble so that they come out of solution and separate from the water in the softener, or by exchanging the dissolved solids in an ion exchange process which leaves the dissolved solids behind in the exchanger.

1. Cold Lime-Soda Softening

In the cold process of lime-soda softening the raw water at room temperature, the softening chemicals (calcium hydroxide and sodium carbonate) and a coagulant are mixed together in a central mixing zone by means of motor driven agitators. As the insoluble compounds, $CaCO_3$ and $Mg(OH)_2$, are produced by the softening chemicals reacting with the scale forming materials namely $Ca(HCO_3)_2$, $Mg(HCO_3)_2$, $CaSO_4$, $MgSO_4$, $CaCl_2$, and $MgCl_2$, a sludge is formed which can be discharged from the bottom of the softener. The coagulant aids in the formation of this sludge. A part of the sludge, however, is kept in suspension by the action of the agitators and the flow of the water, and this forms a sludge blanket through which the water passes on its way to the outlet. The sludge blanket aids in the removal of any impurities not already precipitated from the water.



Cold Lime-Soda Softener

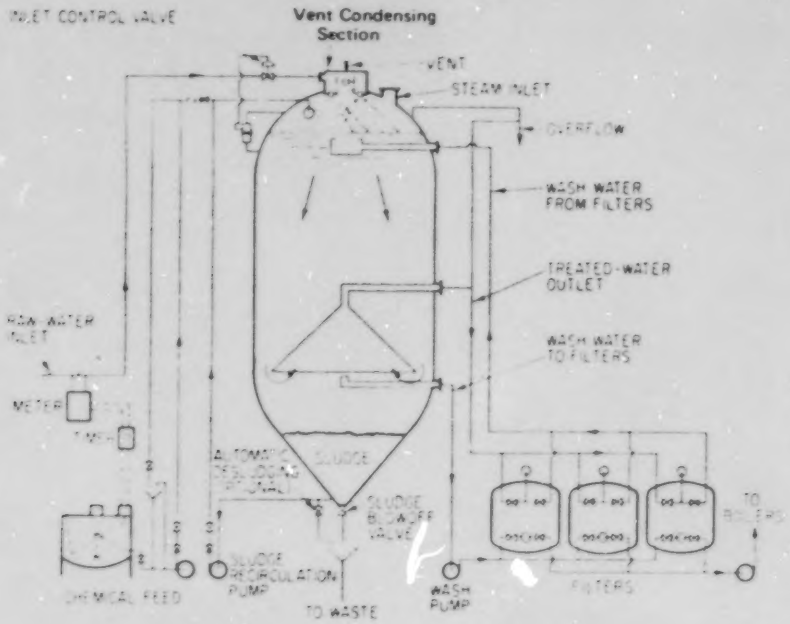
Fig. 5

(PE3-3-12-15)

2. Hot Lime-Soda Softening

In this type of softener exhaust steam is usually used to heat the incoming water to temperatures above 100° Celsius. Chemical reactions in the hot lime-soda unit are the same as for the cold process except that they are almost instantaneous and produce softer water. The hot process lime-soda softener can be used to combine in one complete unit the functions of softening by reducing hardness to 10 - 30 ppm, silica removal, deaeration and filtration. The hot process is most suitable to the softening of high hardness supplies.

Control of lime-soda softening is somewhat more difficult than the control of ion exchange softening and frequent testing and control adjustments are generally required.



Hot Lime-Soda Softener

Fig. 6

Fig. 6 shows the arrangement of a hot process softener used in conjunction with pressure filters which are usually necessary to filter out any carryover of sludge particles from the softener. The process is continuous and carried out in a single tank. A chemical tank and pump with arrangement for proportioning the chemicals to the raw water flow, a sludge recirculating pump and a filter backwash pump complete the essential equipment. Raw water enters the top through a series

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of sprays, the amount being controlled by the level in the softener. Chemicals enter at the same point and are thoroughly mixed by the sprays. Entering steam heats and deaerates the incoming water. Temperature of the process is governed by steam pressure maintained inside the tank. Chemical reactions form calcium carbonate and magnesium hydroxide almost instantaneously. These compounds come out of solution and form a sludge. About one hour retention time is normal, the water flowing downward and under the weir where the sludge is precipitated to the cone chamber below. From the inverted weir an uptake carries softened water to the outlet and to the pressure filters. Periodically some of the sludge is discharged to waste while some of the sludge is continually recirculated which helps to reduce the amount of chemicals needed in the treatment. The filters are arranged to be backwashed with water from the softener and this water is returned to the softener after backwashing.

3. Sodium Zeolite Softening (Sodium Cation Exchange)

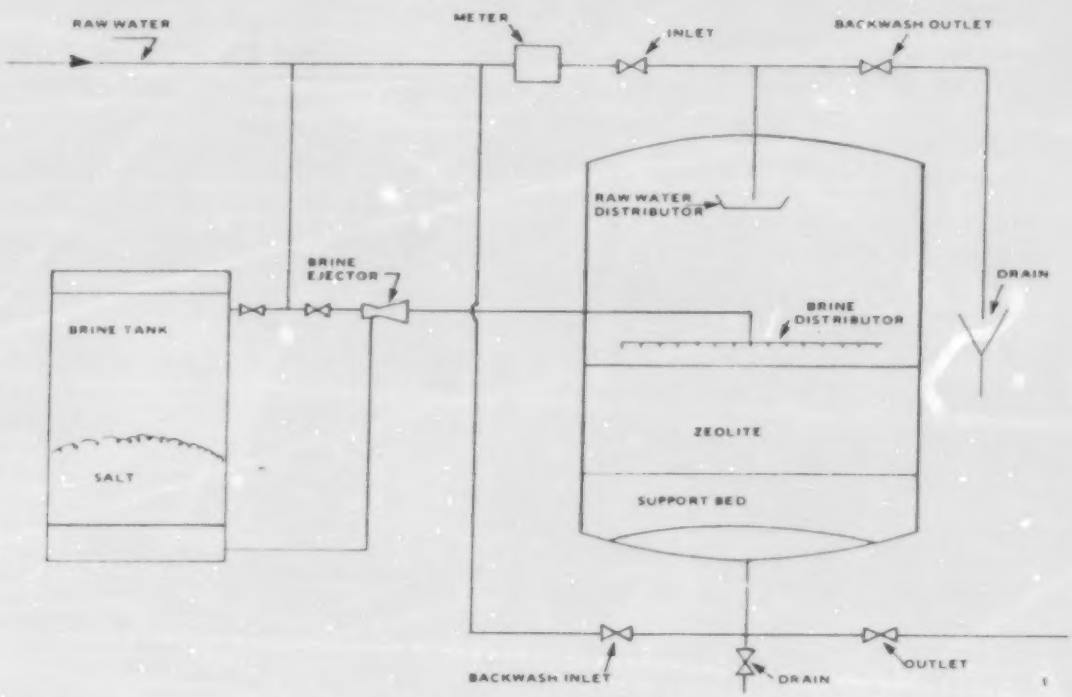
When certain compounds are dissolved in water they disassociate to form positively and negatively charged particles known as ions. The ions which have a positive charge are called cations while those having a negative charge are called anions.

For example, if water contains the scale forming salt calcium sulphate $CaSO_4$ then it will be in the form of calcium (Ca) cations and sulphate (SO_4) anions. If the Ca cations could be exchanged for sodium (Na) cations then the salt would now be sodium sulphate Na_2SO_4 and as this salt is extremely soluble it would not produce scale in a boiler. The same would hold true if the cations of the other scale producing salts could be exchanged for sodium cations. If, as another example, the water also contains the scale forming salt magnesium bicarbonate $Mg(HCO_3)_2$, then this salt will be in the form of magnesium (Mg) cations and bicarbonate (HCO_3) anions. If the Mg cations are exchanged for Na cations then the salt will now be sodium bicarbonate $NaHCO_3$ and as this salt is extremely soluble, as are most of the sodium compounds, it will not produce scale in a boiler.

The sodium zeolite softener uses the principle of ion exchange to remove scale forming salts from the water and to replace them with non-scale forming salts. The softener contains a granular material called zeolite which has the ability, when water is passed through it, to remove the calcium and magnesium cations from the water and to replace them with sodium cations. The Ca and Mg cations are held by the zeolite material which has given up Na cations in exchange for them.

When the zeolite material has given up all its Na cations in exchange for the Ca and Mg cations, it has to be regenerated before it can resume the softening process. The regeneration is done by removing the zeolite softener from service and filling it with a solution of brine (sodium chloride NaCl). The zeolite then absorbs the Na cations from the brine and discards the Ca and Mg cations to the brine. The brine now containing the Ca and Mg cations is then flushed to sewer and the zeolite bed is rinsed out with water. The softener is then returned to service until regeneration is again necessary.

The zeolite may be made up of any one of several materials. Examples of zeolites are natural greensand, synthetic gel, sulfonated coal and styrene resin. It is usually given the chemical formula Na_2Z.



Sodium Zeolite Softener

Fig. 7

(PE3-3-12-18)

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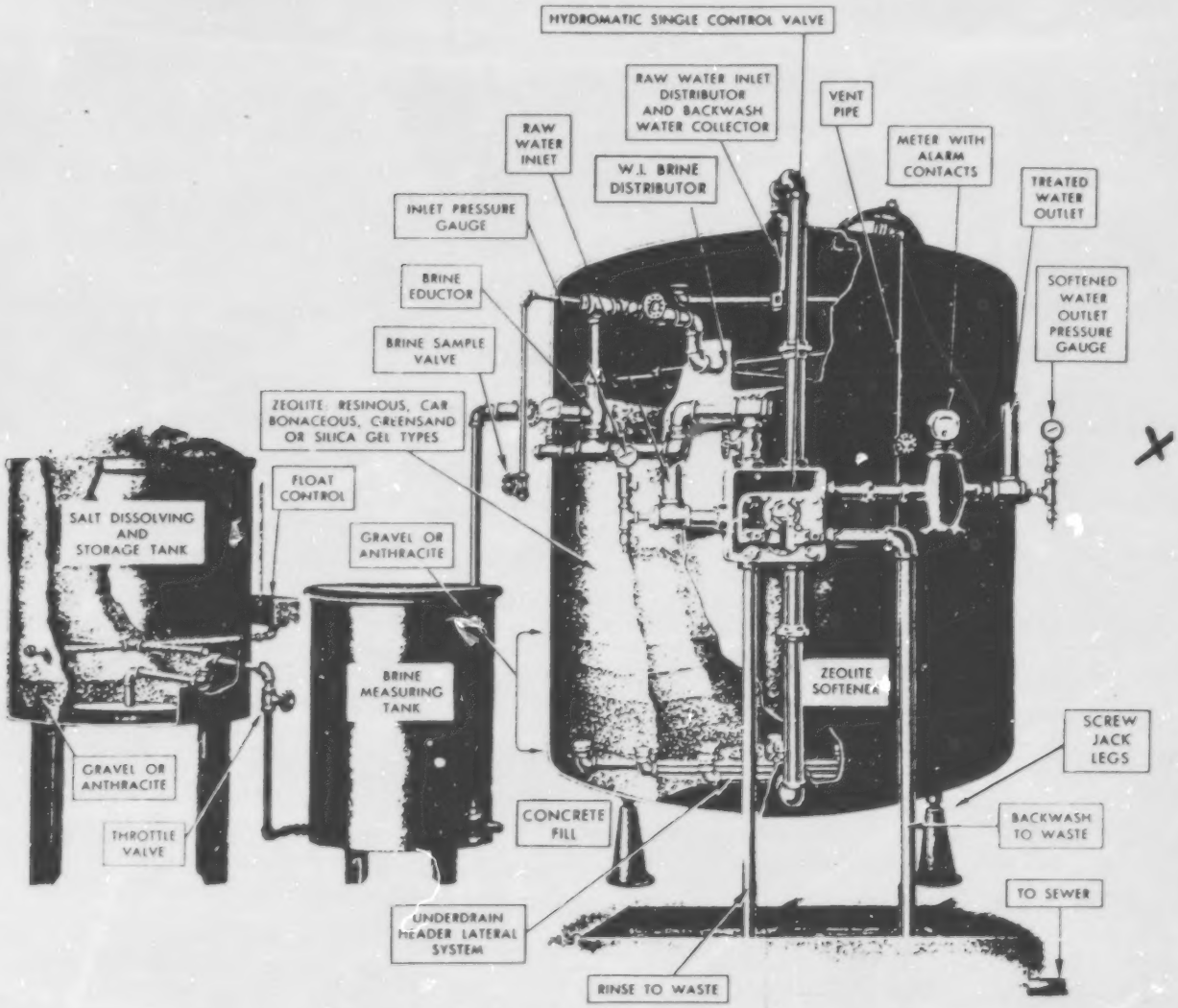
The sketch in Fig. 7 shows the arrangement of the zeolite softener together with a regenerant or brine tank. The zeolite or exchange material is supported on a bed of gravel or anthracite and is contained in a steel pressure tank. The raw water after passing through a meter flows into the top of the softener tank and travels downward through the bed of zeolite and leaves the softener at the bottom.



Zeolite Softener Details

Fig. 8

(PE3-3-12-19)

When the zeolite becomes exhausted, the softener is taken out of service and backwashed by manipulating the valves so that raw water enters at the bottom and flows upwardly through the bed to the wash water collector and then to waste. The backwashing serves to separate and clean the bed and when it is completed the zeolite is regenerated by passing a salt solution or brine into it. This is done by admitting raw water to an ejector or eductor. The water flowing through the eductor produces a vacuum which draws the brine up from the regenerant tank and the brine is then forced into the softener just above the surface of the bed.

After the correct amount of brine has been supplied, the softener is then rinsed by admitting raw water to the top of the softener. This water passes down through the bed rinsing it free of brine and flowing through the drain to waste. After the bed has been completely rinsed of brine, the softener is returned to service once more.

Fig. 8 shows in more detail the piping connections for a zeolite softener. Rather than using several valves to change flow directions during backwash, rinse and regeneration, this type has a master valve which connects together the necessary piping for the various operations when the valve lever is moved to the desired position.

4. Hydrogen Zeolite Softening (Hydrogen Cation Exchange)

In the sodium cation exchange softener, explained in the previous section, the salts of calcium and magnesium were replaced with salts of sodium. While this method does get rid of the scale-forming calcium and magnesium, it does not reduce the total amount of salts dissolved in the water as the sodium salts take the place of the calcium and magnesium salts. One of these sodium salts, sodium bicarbonate, will decompose in the boiler into sodium carbonate, sodium hydroxide and carbon dioxide. The sodium hydroxide may cause embrittlement of the boiler metal and the carbon dioxide will be carried over with the steam and form carbonic acid in the return lines which results in corrosion. Sodium bicarbonate will also tend to cause the water in the boiler to foam.

If instead of a sodium zeolite softener, a hydrogen zeolite softener is used then the scale forming salts will be removed without the formation of sodium bicarbonate. Hydrogen zeolite has the ability to remove calcium, magnesium and sodium cations from the mineral salts and replace them with hydrogen ions. As a result the mineral salts are converted to acids. These acids are subsequently neutralized by the use of an alkali or base such as caustic soda NaOH, or in some cases the acid-containing water from the hydrogen zeolite softener is mixed with the water from a sodium zeolite softener and this will also result in the neutralization of the acids.

(PE3-3-12-20)

Regeneration of the hydrogen zeolite is accomplished by the use of an acid solution which restores hydrogen ions to the zeolite and removes the calcium, magnesium and sodium cations from the zeolite.

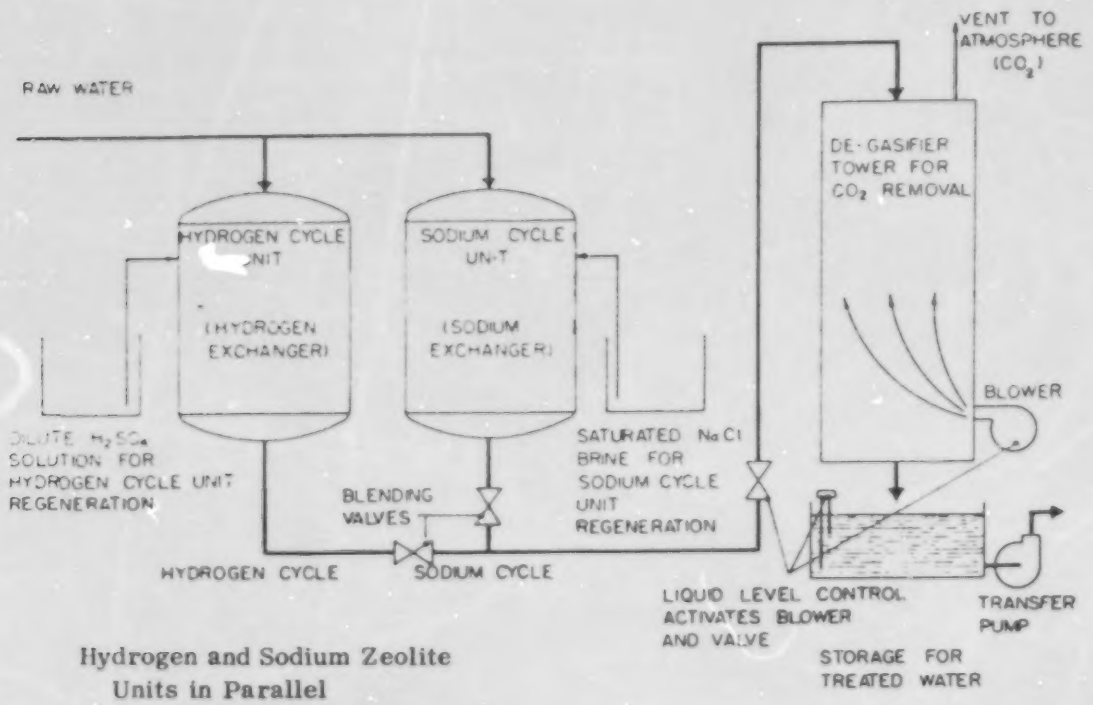
The material used in the hydrogen zeolite softener may be lignite, sulphonated coal, coke or synthetic resin.

The effluent or discharge from a hydrogen zeolite softener contains various acids which would be corrosive to the metal in the piping and the boiler. Therefore these acids must be either neutralized or removed from the effluent. In the case of carbonic acid H_2CO_3, it quickly breaks down into water and carbon dioxide as illustrated in the following equation.

Carbonic acid ⟶ Water + Carbon Dioxide

$$H_2CO_3 \longrightarrow H_2O + CO_2$$

The CO_2 can be removed by passing the water through a degasifier tower in which the water flows down over trays and is scrubbed by upward flowing air from a blower.



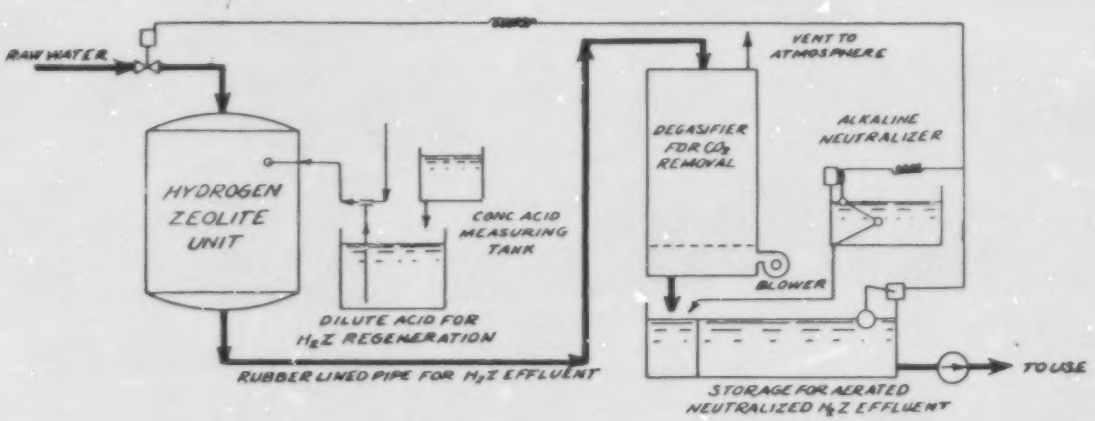
Hydrogen and Sodium Zeolite Units in Parallel

Fig. 9

(PE3-3-12-21)

An arrangement involving the use of a degasifier and a sodium zeolite unit in conjunction with a hydrogen zeolite softener is shown in Fig. 9. Before entering the degasifier, the effluent from the hydrogen zeolite unit is mixed with the effluent from a sodium zeolite unit in order to neutralize the sulphuric and hydrochloric acids resulting from the hydrogen ion exchange. Also if silicic acid is present it will also be neutralized.

Another arrangement which uses an alkali, such as sodium hydroxide NaOH, to neutralize the acid effluent from a hydrogen zeolite unit is shown in Fig. 10.



Hydrogen Zeolite with Alkaline Neutralizer

Fig. 10

The neutralization of the acid effluent by the sodium hydroxide is shown in equation form as follows:

1. Sulphuric Acid + Sodium Hydroxide ⟶ Sodium Sulphate + Water

$$H_2SO_4 + 2\,NaOH \longrightarrow Na_2SO_4 + 2H_2O$$

2. Hydrochloric Acid + Sodium Hydroxide ⟶ Sodium Chloride + Water

$$HCl + NaOH \longrightarrow NaCl + H_2O$$

3. Silicic Acid + Sodium Hydroxide ⟶ Sodium Silicate + Water

$$H_2SiO_3 + 2\,NaOH \longrightarrow Na_2SiO_3 + 2H_2O$$

(PE3-3-12-22)

The sodium sulphate and sodium chloride contained in the neutralized water are very soluble and do not tend to produce scale in the boiler. The sodium silicate, however, will produce extremely hard scale in the boiler and must be gotten rid of by some other method.

5. Demineralization (Cation and Anion Exchange)

An advantage of the hydrogen zeolite process over the sodium zeolite process is that the hydrogen zeolite removed the sodium bicarbonate and thus reduced the dissolved solids content of the water. The acids in the effluent from the hydrogen zeolite unit, such as sulphuric and hydrochloric, were then neutralized. However when these acids were neutralized, the anions of these acids, such as SO_4 and Cl, combined with the sodium from the neutralizing base NaOH and formed sodium suiphate and sodium chloride. While these sodium salts do not tend to form scale, they may cause foaming in the boiler and require excessive blowdown. In addition to this disadvantage, the hydrogen zeolite unit will not remove any silica present in the water.

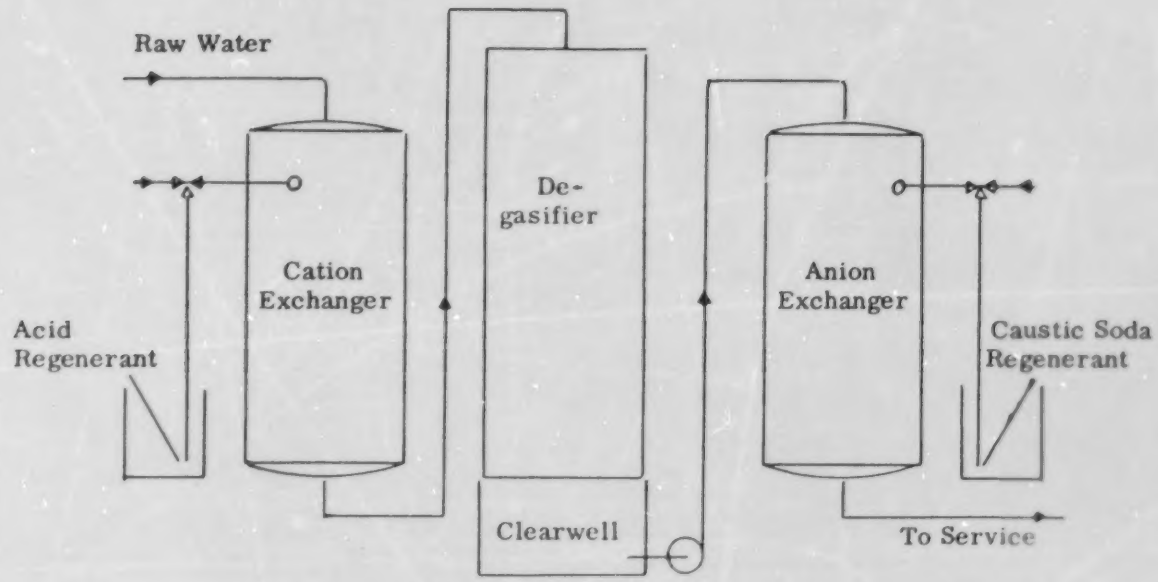
If it is desired to remove all the mineral salts from the water, a process known as demineralization or deionization is used. This involves using a hydrogen zeolite cation exchanger to remove the sodium, magnesium and calcium cations and then using an anion exchanger to remove the sulphate, chloride and silica anions. In addition, a degasifier is used to remove any carbon dioxide present. The effluent from the demineralizing process is water that is free from all mineral impurities and is equal in quality to distilled water.

The hydrogen zeolite cation exchanger has already been described in the previous section.

The anion exchanger contains a hydroxide resin material which has the ability to remove the anions of the acids contained in the effluent from the cation exchanger. This anion exchange material is regenerated with sodium hydroxide when it becomes exhausted.

A demineralizing arrangement is shown in Fig. 11.

The raw water first passes through the cation exchanger where the cations of calcium, magnesium and sodium are removed and acids formed. As a result the effluent from the cation exchanger now contains carbonic, sulphuric and hydrochloric acid. In addition, if any silica was present in the raw water it will now be in the form of silicic acid H_2SiO_3.



Demineralizing Arrangement

Fig. 11

The carbonic acid in the cation exchange effluent breaks down into water and carbon dioxide and this carbon dioxide is removed as the effluent passes through the degasifier.

The effluent is then pumped to the anion exchanger where the acid anions are removed leaving pure demineralized water which then passes to service.

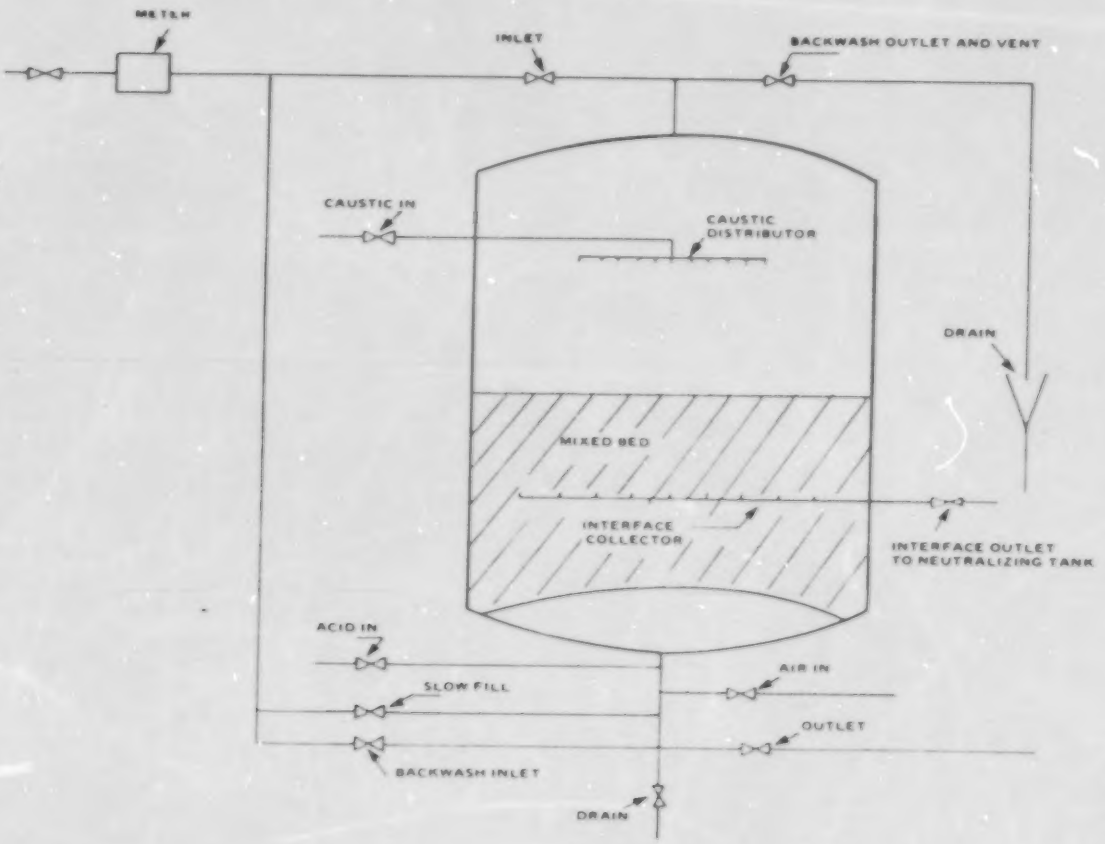
When the exchangers become exhausted they must be backwashed, regenerated, rinsed and then returned to service.

The cation exchanger is regenerated with a solution of sulphuric acid and the anion exchanger is regenerated with a solution of sodium hydroxide.

When a demineralizing system is used it is important that the raw water supplied to the system has first been filtered to remove any suspended materials. If this is not done then the suspended materials will be trapped in the exchange material and will form a coating thus reducing the flow of cations and anions.

(PE3-3-12-24)

A special type of demineralizing system as shown in Fig. 12 combines the cation exchange material with the anion exchange material in a single shell. This is called a mixed bed system as the two exchange materials are mixed together in a single bed. When regeneration is necessary, the two materials are separated by backwashing. The backwashing causes the lighter anion exchange material to rise to the top of the bed with the heavier cation exchange material forming the bottom layer. Then each layer is regenerated and rinsed. The two materials are then mixed together again by blowing air upwardly through the bed.



Mixed Bed Demineralizer

Fig. 12

(PE3-3-12-25)

Thermal Methods

Treating water thermally is probably one of the oldest methods of external water treatment. Heat can soften, but the use of heat to soften water will normally depend on the availability of exhaust steam to be economical. The most common purpose of heat in water treatment is to degasify the water thereby reducing corrosion in the boilers.

1. Deaerators

The construction of a deaerator usually involves four sections; a section where the water is heated to the boiling point, a section where the released gases are scrubbed from the water, a section for the storage of the deaerated water and a section for condensing any steam that is being carried to the vent with the released gases.

Deaerators are classed as spray type or tray type.

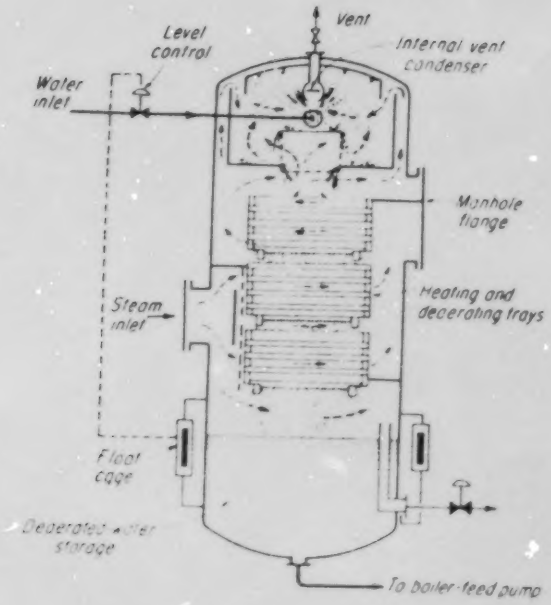
In the spray type the entering water passes through spray valves and is therefore in a finally divided state. It is then heated by coming in contact with steam in the heating section. The water then passes to the scrubber section where it is scrubbed by the entering steam and the gases released by the heating are removed. The deaerated water then passes to the storage section and the steam flows from the scrubbing section to the heating section where it heats the incoming water spray and where most of it condenses. The gases released in the scrubbing section flow to the vent condensing section where any steam present is condensed and the gases are cooled to some extent. The gases then pass out through the vent.

In the tray type deaerator the process is much the same except that the water, instead of passing through spray nozzles, is broken up by trickling down over a series of trays. The entering steam scrubs the water in the lower tray section and heats the water in the upper tray section. The released gases and some steam pass to the vent condensing section where the steam is condensed and the gases pass to the atmosphere through the vent opening.

Some deaerators combine the spray and tray principles with the water first being sprayed into the deaerator and then trickling over a series of trays. This combination type is illustrated in Fig. 13.

In this combination type the released gases must pass through the spray of incoming water on their way to the vent opening. In this way any steam carried with the gases will be condensed. This section of the deaerator is called the in-

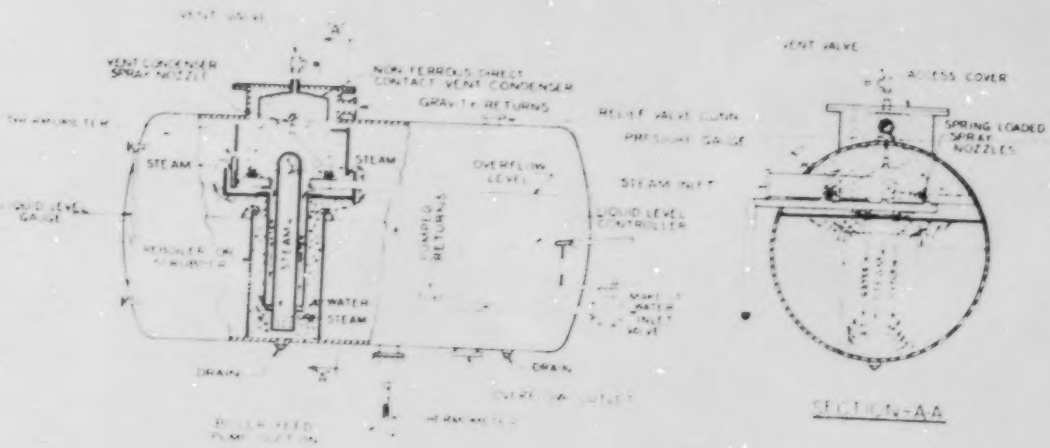
ternal vent condenser.



Combination Spray
and
Tray Deaerator
Fig. 13

The level in the storage section is regulated by float controlled inlet and overflow valves.

One design of spray deaerator is illustrated in Fig. 14.



Spray Deaerator
Fig. 14

(PE3-3-12-27)

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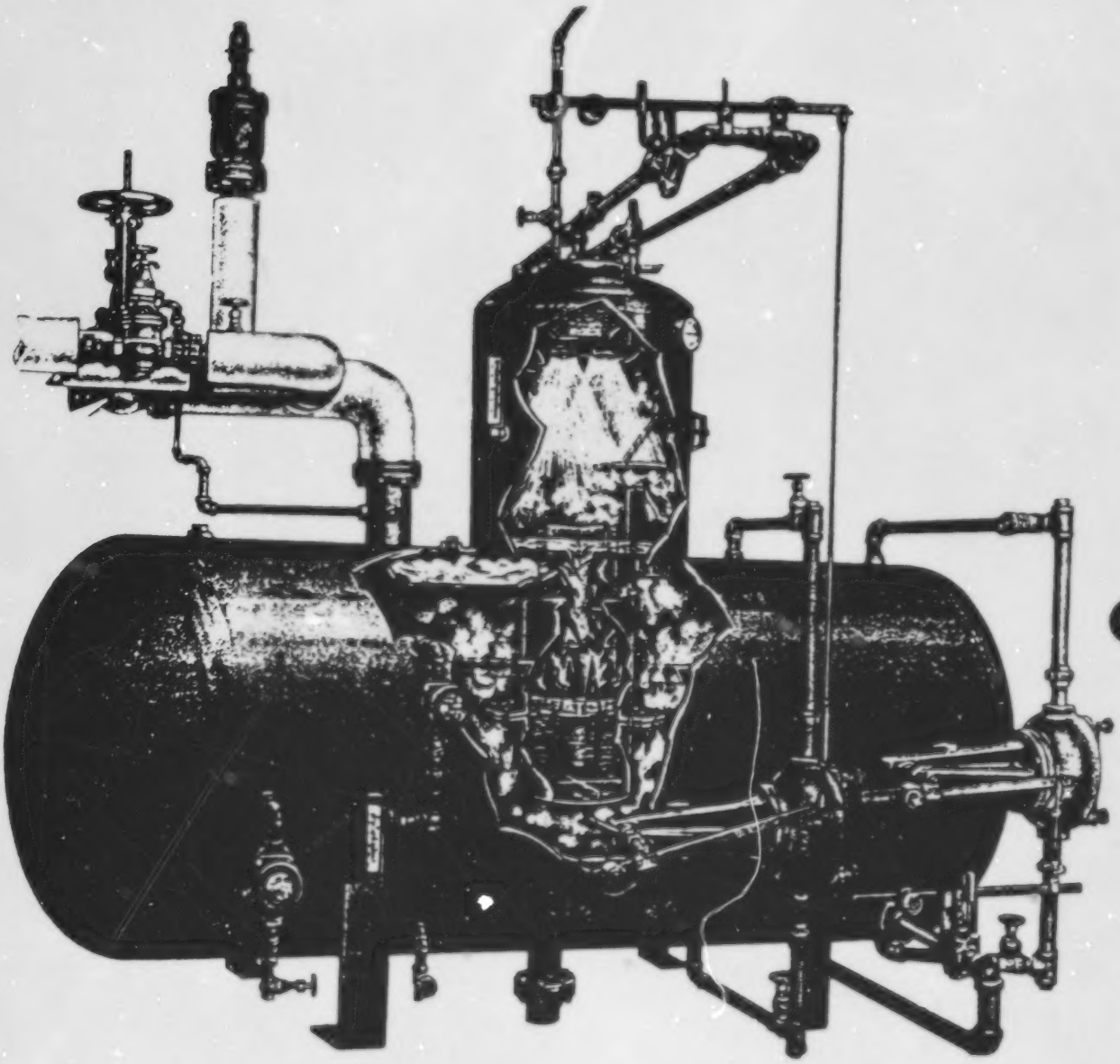


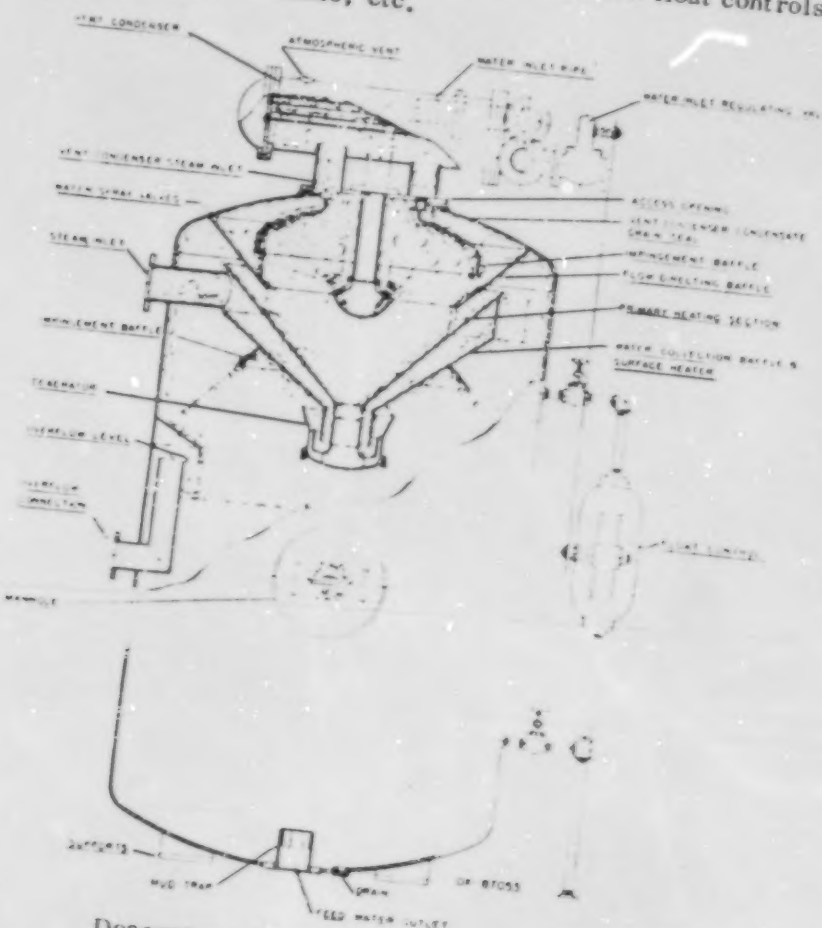
Spray Deaerator
(Outside View)

Fig. 15

(PE3-3-12-28)

The inlet water enters the heater compartment through upward angled spray nozzles and is heated by steam rising from the scrubber compartment. The heated water then flows down into the scrubber section where it is scrubbed by the steam entering through a central pipe. The steam and the gases scrubbed from the water then rise through the heating compartment, where most of the steam is condensed, to the vent condenser chamber. Another water spray in this chamber condenses any remaining steam and the gases then pass out through the vent.

An outside view of another design of spray deaerator appears in Fig. 16 and shows the various fittings such as inlet and overflow float controls, thermometers, pressure gage, manhole, etc.



Deaerator with External Vent Condenser

Fig. 16

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The deaerators shown in Figs. 13, 14 and 15 all feature direct contact vent condensers. That is to say, the water used to condense the steam carried by the venting gases comes in direct contact in the form of a spray with the steam. These vent condensers are also called internal vent condensers as they are located within the shell of the deaerator.

The deaerator shown in Fig. 16 features an external vent condenser. This condenser is located outside of the shell and the venting gases and steam do not come directly in contact with the water. Instead, the cool incoming water passes through tubes within the vent condenser and the venting gases and steam pass over the outside surface of these tubes. As a result the steam is condensed and flows back as condensate into the deaerator.

The steam used for heating and scrubbing of the water in most types of deaerators is exhaust steam from some source. If exhaust or waste steam is not available then live steam can be used after reduction of pressure.

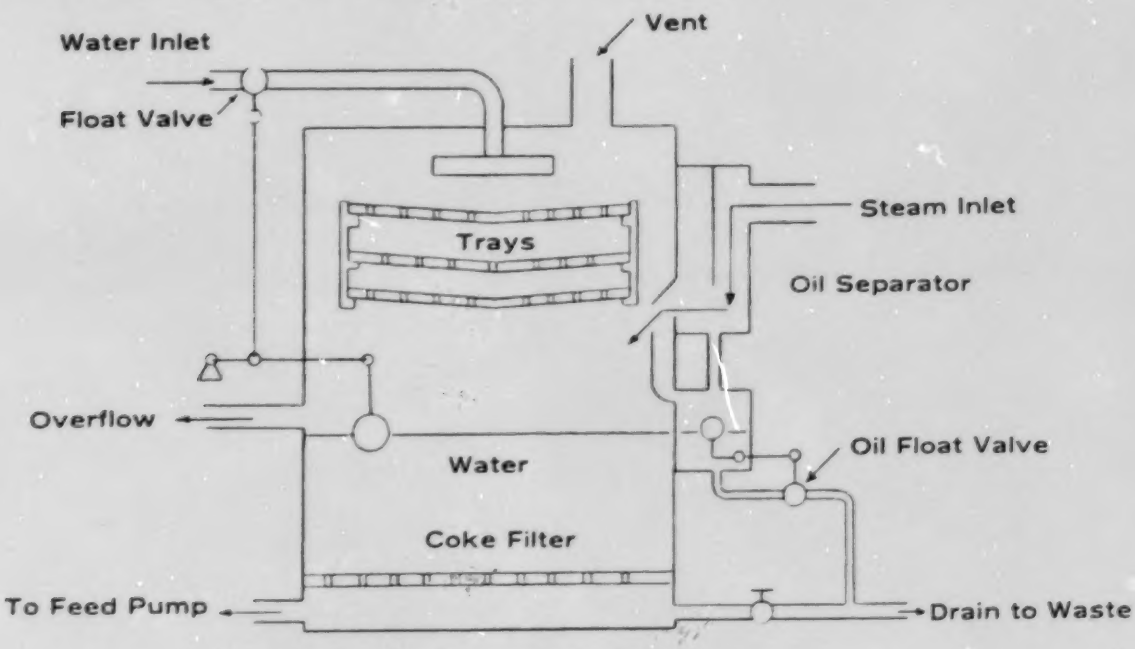
Usually the operating pressure of the deaerator is about 70 or 100 kPa but pressures as high as 1200 kPa are often used. For example in an electrical generating station, the deaerator is usually supplied with steam which has been bled off from the turbine and in this case the pressure may be as high as 1200 kPa or even higher.

In some cases the deaerator is designed to operate under a vacuum. The vacuum is usually produced by a steam jet ejector but in some types by a mechanical vacuum pump. By reducing the pressure in the deaerator, the water can be made to boil at comparatively low temperatures. If, for example, the pressure in the deaerator is reduced to 50 mm of mercury then the water will boil at about 38° C. Vacuum deaerators are not as efficient as those operating at pressures above atmospheric.

2. Open Feedwater Heaters

Open feedwater heaters are heaters which are open to the atmosphere and certain limitations are thereby placed upon them. The pressure obviously cannot be more than atmospheric, the temperature cannot exceed the boiling point of water or 100° C and they must be placed on the suction side of the boiler feedpumps. Because of their placement, the boiler feedpumps tend to vaporlock and lose suction easily which is one reason why they are now seldom installed. They were popular in plants with steam engines because an oil separating section was normally combined with this heater to separate cylinder oil from the engine condensate. In addition to heating the water open heaters serve the purpose of

softening, deaerating and filtering the water. The softening takes place when bicarbonates break down into CO_2 and carbonates when heated. The CO_2 is released to atmosphere while the carbonates which are much less soluble settle out in the heater. Because bicarbonates can be removed by heating in an open heater before they reach the boiler, they are often referred to as temporary hardness, while sulphates, chlorides and nitrates which cannot be removed in this manner are referred to as permanent hardness. Fig. 17 shows a typical open feedwater heater. In most cases exhaust steam is used to heat the water.



Open Feedwater Heater

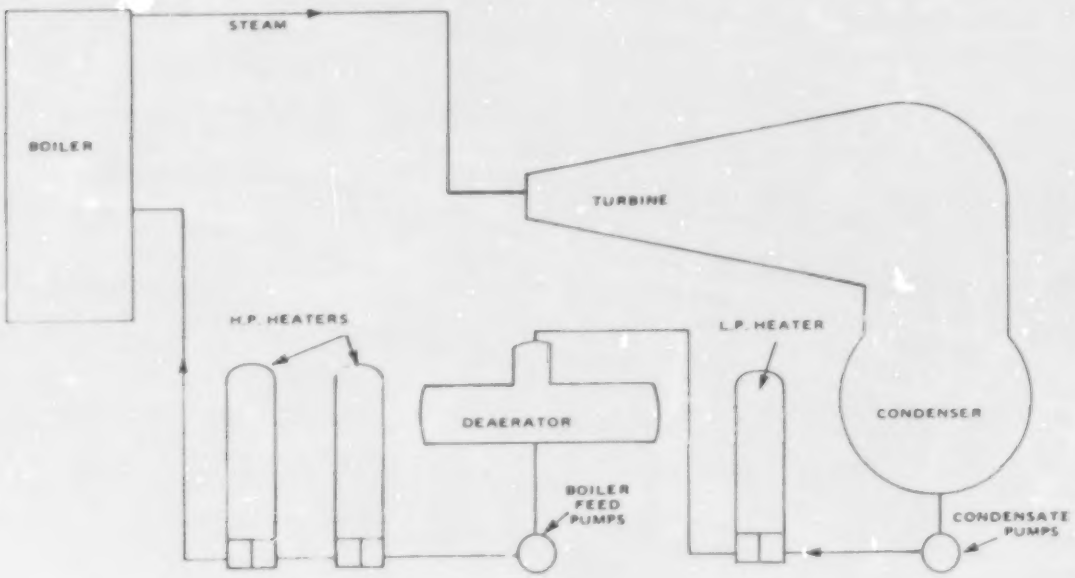
Fig. 17

3. Closed Feedwater Heaters

As the name implies, closed feedwater heaters are not open to the atmosphere and the steam does not come in direct contact with the water. Being closed this heater may be placed anywhere in the plant cycle including the discharge of the boiler feedpumps. This allows the water to be heated to much higher temperatures than in an open heater and by doing so the overall plant efficiency is often increased. Increasing plant efficiency is the main role of closed feedwater heaters but they can also be used to soften the water in some cases by precipitating hardness from the water before it reaches the boiler. When used in this capacity two or more heaters must be placed in parallel so that one can be removed from service to be cleaned while others remain in service.

(PE3-3-12-31)

Fig. 18 shows typical locations of closed feedwater heaters in a steam plant. The heat medium is often bled steam from various turbine stages. Fig. 19 shows the construction of a closed feedwater heater.



Closed Feedwater Heater Locations

Fig. 18

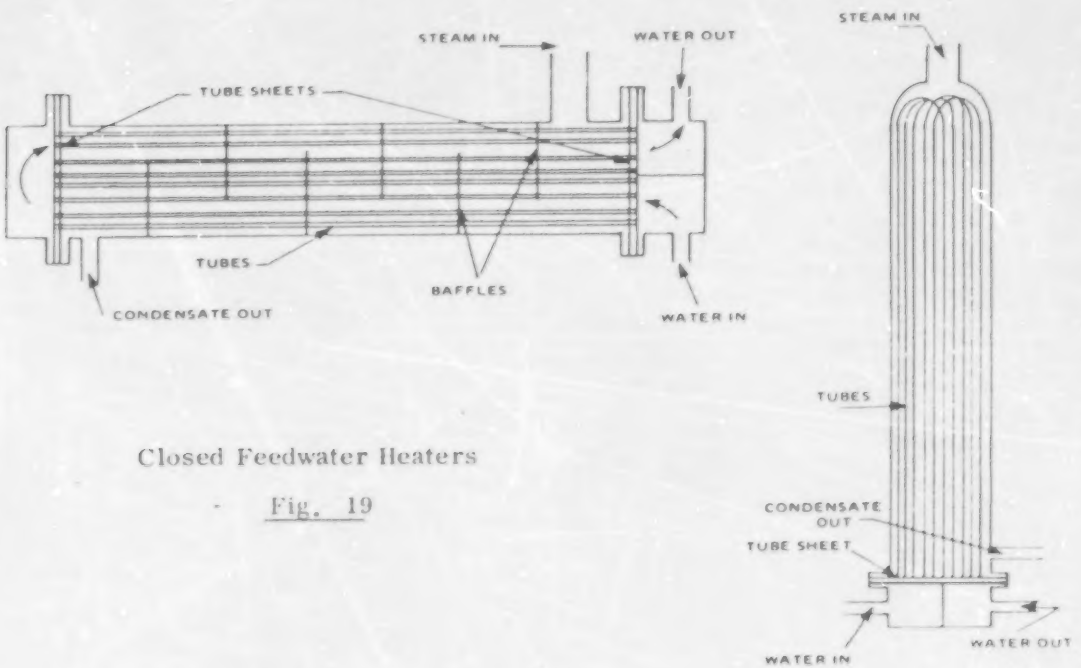
4. Evaporators

Boilers or steam generators which operate at high pressures and temperatures require make-up water that is free from any impurities. This pure water may be obtained through the use of demineralizers to remove the dissolved solids and deaerators to remove the dissolved gases. Another method which is commonly employed in central stations is to use evaporators instead of demineralizers to obtain water free from dissolved solids and then to use deaerators to remove the dissolved gases.

The process which takes place in the evaporator is simply the boiling of the water. The steam or vapor produced from this boiling will be free from solids and when subsequently condensed will form solids - free water or distilled water.

However, any dissolved gases present in the original water will pass off with the steam in the evaporator and consequently the distilled water must be deaerated before going to the boiler. The impurities left behind in the evaporator will form scale and therefore the water fed to the evaporator is usually softened in order to reduce the amount of scale formed. In addition the evaporator must be blown down either continuously or intermittently in order to reduce the concentration of solids in the water within the evaporator.

The heat necessary to boil the water in the evaporator is usually provided by exhaust steam or steam bled from a turbine stage. This steam flows through a set of tubes contained within the evaporator. The water which surrounds the tubes is thus heated.



Closed Feedwater Heaters

Fig. 19

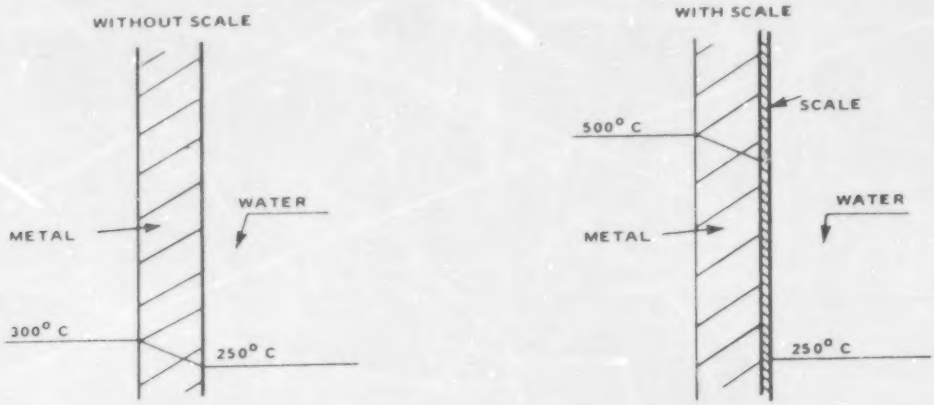
(PE3-3-12-33)

INTERNAL WATER TREATMENT

Internal water treatment is the treatment of water after it has entered the boiler. Since this water has now become boiler water is may properly be termed boiler water treatment. The methods of clarifying, softening and degasing have been discussed but no system of external treatment, regardless of a high degree of efficiency, is in itself adequate protection for the boiler and associated equipment. In all cases the feedwater will remain imperfect in some small way which always necessitates the use of internal treatment. The main objective of all water treatment is elimination of the troubles caused by scale and mud, carryover, corrosion and embrittlement. The methods employed in combating these problems by internal treatment are discussed below and listed in the chart on Page 35.

Scale and Mud Deposits

Preventing scale and mud from forming in a boiler is important for two basic reasons: a) scale and mud cause metal overheating and b) they can contribute to boiler corrosion. As water circulates through boiler tubes it absorbs, heat and cools the metal. Deposits form a barrier between the circulating water and the metal, decreasing the efficiency of heat transfer. As the result, the metal has to be hotter to transfer the same amount of heat as clean metal. When boiler steel is heated to about 500° C it starts to weaken. Keeping deposits at a minimum is therefore important in preventing metal overheating.



Effect of Scale on Metal Temperature

Fig. 20

(PE3-3-12-34)

INTERNAL WATER TREATMENT CHART			
PROBLEM	METHOD	CHEMICALS USED	REMARKS
Scale and Mud Deposits	Precipitation in cool areas	Soda (Na_2CO_3) Caustic (NAOH) Phosphate (NA_3PO_4)	Preferred Precipitates: $CaCO_3$, $Mg(OH)_2$, $Ca_3(PO_4)_2$, $MgSiO_2$
	Sludge Conditioning	Tannins Lignins Starches	for Carbonates and Hydroxides for Phosphate and Iron Solids for Silica and Oil
	Blowdown	----	always needed in conjunction with other methods
	Chelating	EDTA NTA	
Carryover	Priming Control	----	
	Misting Control	----	install steam separator and driers
	Foaming Control	Antifoams	lower solids in boiler water
Corrosion	pH Control O_2 and CO_2 Removal	Caustic, Phosphate Sodium Sulphite, Hydrazine Amines	
Embrittlement	pH Control Avoid Stresses	Caustic, Phosphates ----	

Deposits can foster corrosion by isolating metal from contact with water which in some instances develops the isolated metal into an anode with loss of metal the result. Or evaporation of boiler water which seeps under deposits can produce a concentrate of caustic which is capable of eating into very hot metal under stress causing actual pits or craters to form in the metal under the deposits.

Internal treatment to prevent boiler scale is needed in all cases, even if the feedwater is pre-softened. One ppm of feedwater hardness adds up to about 500 kg of potential scale a year in a boiler making 5000 kg of steam per hour.

(PE3-3-12-35)

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The basic approach in combating scale and mud from depositing involves:

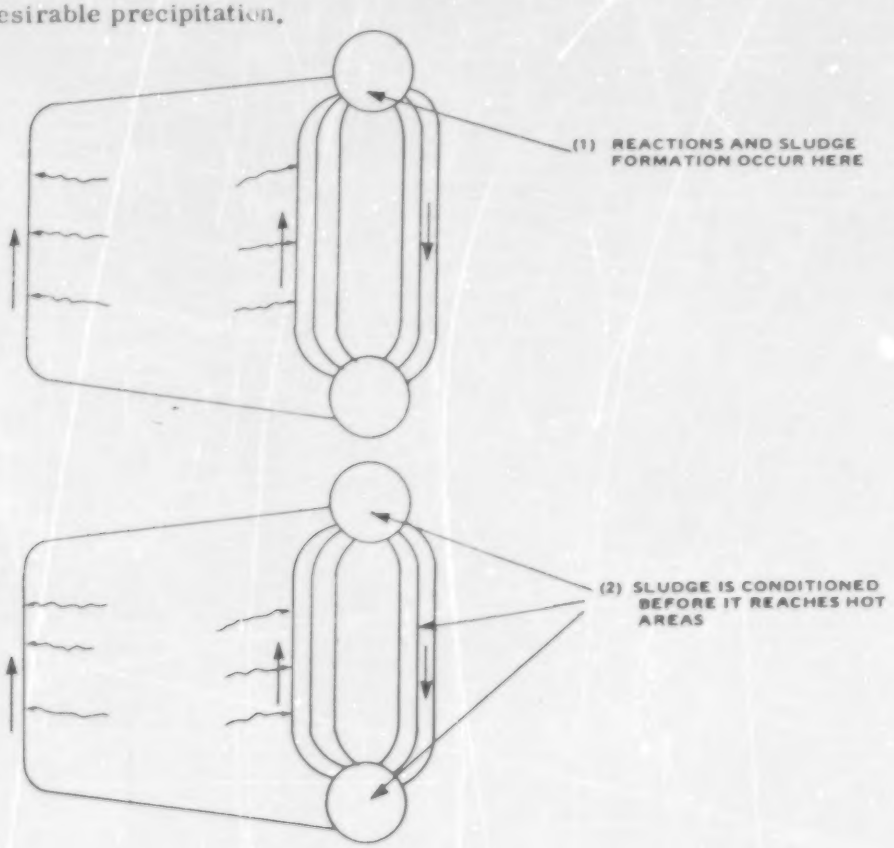
1) forcing the hardness to come out of solution and be suspended in the water rather than be deposited out directly on boiler metal,

2) condition or treat the suspended solids so that they will not stick to boiler metal and

3) remove excess suspended solids by blowdown.

All this needs to be done in the cooler areas of the boiler where the feedwater enters, before it circulates to the hot boiler areas.

Treatment against scale deposits, in general, aims to precipitate hardness so that the suspended solids formed are easy to condition. Some of the desirable forms of precipitated hardness are: calcium carbonate, calcium phosphate, magnesium hydroxide and magnesium silicate. Therefore soda ash, caustic soda and various forms of sodium phosphate are commonly used because they produce desirable precipitation.



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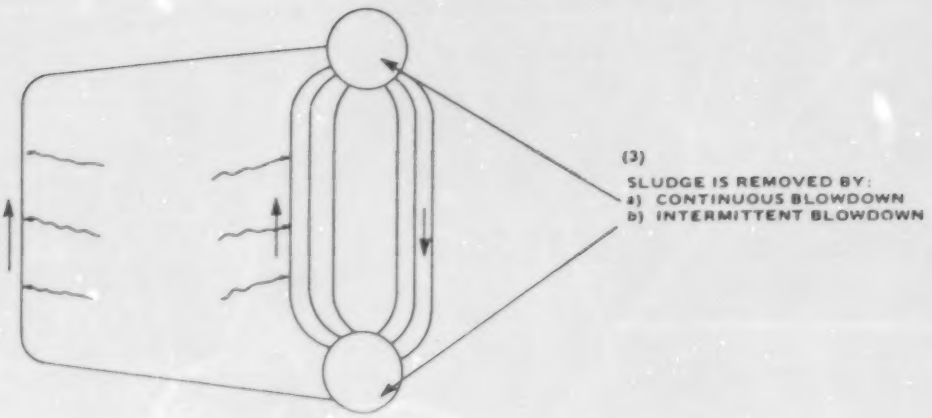


Three Stages in Scale Prevention

Fig. 21

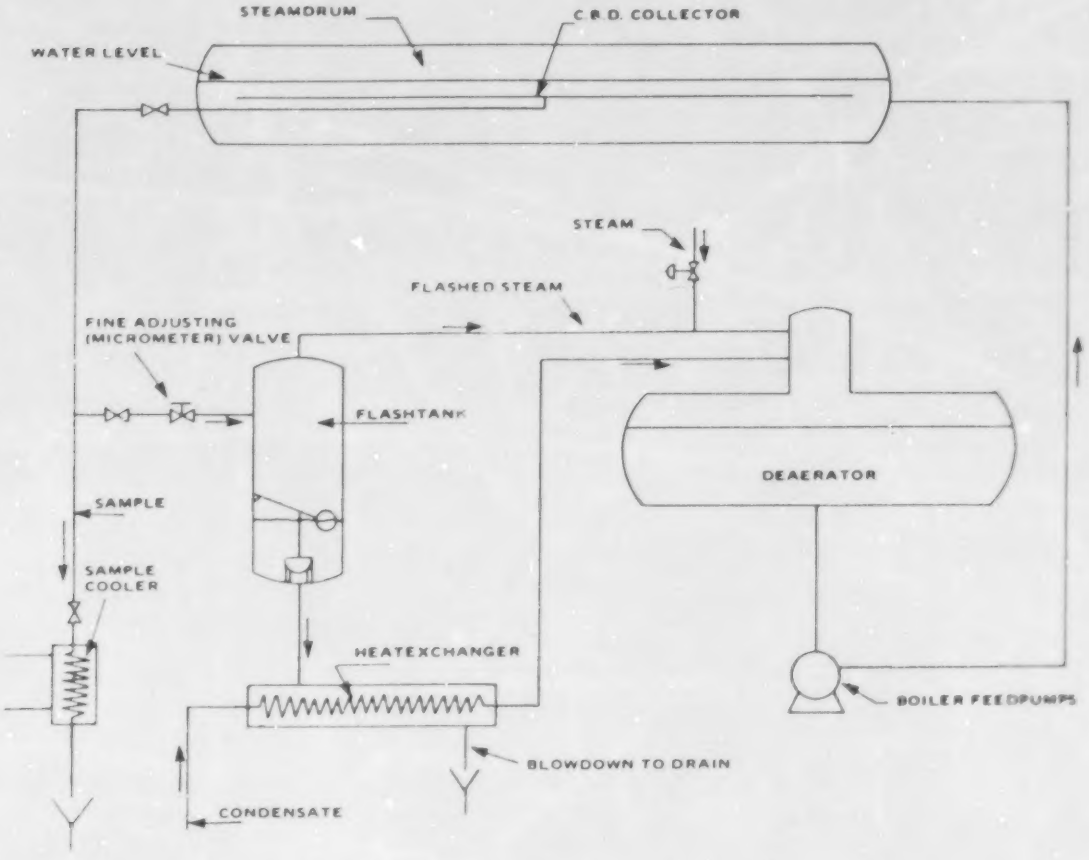
For sludge conditioning, specially processed, temperature stable organics are used which can be classified as (1) tannins - effective in producing a non-sticky sludge, (2) lignins - causing the suspended solids to be coated making the particles non-adherent and (3) starches - used where silica is a problem.

After the solids in the feedwater have been precipitated and conditioned they must be removed otherwise a gradual build up of solids would occur.

To hold boiler water solids at a steady level, the amount removed by blowdown must equal the amount brought in by the feedwater. The level of solids that can be tolerated in a particular boiler depends mainly on boiler pressure. Maximum limits are set by the American Boiler Manufacturers Association (A.B.M.A.) in Table 1 on Page 4. These limits may be used in determining blowdown needs. Testing for boiler water dissolved solids is often done with a conductivity meter.

All boilers are equipped with blowdown piping from the lower parts of the boiler where sludge is apt to collect (mud drum, lower headers, etc.). This piping allows manual or intermittent blowdown which is essential and important in most cases. It is, however, not efficient in maintaining a consistent level of solids in the boiler water. For this reason continuous blowdown is often used. Continuous blowdown provides a more consistent solids level thereby lowering the danger of scale formation. This system also lends itself to recuperating some of the heat from the water blown down giving better fuel economy. Most continuous blowdown systems consist of a perforated collecting pipe in the steam

drum near the discharge from the risers (generating tubes) and away from the feedwater inlet, a measuring or metering valve to regulate the amount of blowdown and a low pressure flashtank where some of the water flashes into steam which is used as a heat supply for the deaerator. A typical continuous blowdown system is shown in Fig. 22.



Continuous Blowdown System

Fig. 22

While blowdown is a basic part of any internal treatment program, excessive blowdown is costly as it wastes fuel and water. Good control of blowdown is therefore very important.

(PE3-3-12-38)

One additional method of combating scale involves the use of chelating agents. These agents have the ability to tightly hold the metal ions in a soluble compound which does not deposit on hot boiler surfaces. The use of chelating agents can give better results than conventional treatment in some cases but accurate control must be provided when they are used. The cost of agents such as EDTA and NTA is high so that they are not normally used unless the feedwater hardness is less than 2 ppm. If proper feeding points, sample points and good analytical control are not available, chelating agents present a potentially severe corrosion hazard.

Carryover

Carryover of water into the steam lines can occur when the boiler water primes, mists or foams. Priming is a condition where water is "lifted" into the steam lines with the steam during high water levels or sudden load increases or when the steam separating equipment in the steam drum is broken or otherwise inoperative. Misting is a carryover in the form of a fog-like mist which is caused by tiny water particles that are thrown off by the water as steam bubbles burst on the surface. Misting is not caused by boiler water solids or chemical conditions and can only be prevented by effective steam separating equipment such as separators, washers or dryers.

Foaming or frothing occurs when the concentration of certain types of dissolved and suspended solids in the boiler water is too high. The impurities strengthen the film around the steam bubbles so that they do not readily burst at the water surface and form a froth. This froth becomes entrained in the steam. To prevent foaming the solids in the boiler water must be controlled. Chemically, foaming can be prevented by the use of antifoams which weaken the bubble film, causing the bubbles to burst easily.

Carryover is very undesirable because it will cause deposits in superheaters and steam driven equipment. Severe carryover may cause costly and dangerous damage to turbines and engines.

Corrosion

Protection against corrosion is extremely important because once metal has corroded or disappeared, the damage done is irreparable. The two major contributors to corrosion are a low pH (acid dissolves iron) and dissolved oxygen. CO_2 can cause a low pH because it forms carbonic acid but CO_2 also speeds up the corrosive action of oxygen. Oxygen is roughly five to ten times more corrosive than carbon dioxide. But the two gases acting together are 10

to 40 percent more corrosive than the same quantity of the two gases acting separately. A high enough pH is normally established during the control for scale and sludge for which soda ash, caustic soda or phosphates are used. Sodium sulphite ($Na_2 SO_3$) is commonly employed to scavenge oxygen from water in low pressure boilers while hydrazine ($N_2 H_4$) is mostly used in high pressure boilers. These chemicals may be fed to the storage section of the deaerator so that high pressure feedwater heaters and economizers are also protected.

Corrosion of return lines is another common occurrence because carbon dioxide may be released in the boiler by the decomposition of bicarbonates and air may leak into return lines, particularly in vacuum and gravity systems.

To prevent corrosion of return lines, chemicals may be fed to the boiler which pass off with the steam and either neutralize and raise the pH of the condensate or else form a film over the return line surfaces and thus prevent corrosion. The chemicals are known as amines and in the first case are called neutralizing amines and in the second case are called filming amines.

Embrittlement

On Page 3 of this lecture caustic embrittlement was discussed. Embrittlement prevention involves exact control of pH, the importance of which increases with boiler pressure. In high pressure boilers a precise method of control called "co-ordinated phosphate control" is often used to eliminate free caustic and the possibility of embrittlement.

CHOICE OF WATER TREATMENT

In general, as boiler pressures increase, improved feedwater quality is required. Lower pressure boilers are often able to use raw water make up with only internal treatment. High pressure boilers at the other end of the scale may require external treatment of the makeup water which removes all dissolved solids. And there are all degrees of feedwater treatment in between these extremes. Lower pressure boilers up to about 1200 kPa need external treatment only when suspended solids in the boiler will be too high. When makeup is low or the raw water soft, internal treatment will likely be able to handle the job alone. When makeup is high or the raw water hard, a lime soda softener with filters to lower the hardness to about 25 ppm is likely needed. If practical, a deaerator should be included in the feedwater cycle to remove dissolved oxygen and CO_2.

Boilers operating over 1200 kPa nearly always require some type of external treatment and a deaerator is a must. Lime soda softeners are able to remove large quantities of hardness but the hardness of the effluent is still 20 ppm or higher. Ion exchange softeners cannot remove large quantities of hardness but the effluent of a zeolite softener is 1 - 2 ppm while the effluent of a demineralizer approaches zero hardness. The degree and type of treatment system will vary with the percent makeup, raw water hardness and overall economics. The cost of chemicals, installation, maintenance, depreciation, etc., all must be taken into consideration. The type of equipment which provides optimum results with minimum cost will obviously be the best choice.

Table 1 on Page 4 of this lecture gives a suggested maximum limit of feedwater solids for boilers operating at different pressures. From this table it is obvious that a lime soda softener would not provide adequate treatment for boilers operating at pressures over 2400 kPa while a zeolite softener becomes inadequate for boilers over 7000 kPa. A combination of lime soda followed by filters and ion exchange is a likely choice for high pressure boilers with hard make up water, the lime-soda being used to remove the bulk of the hardness while the ion exchange is used to lower the hardness of the lime-soda effluent further to the level required.

TESTING METHODS

In order to determine the nature and amount of the impurities in the boiler water or in the feedwater, it is necessary to obtain samples of this water and subject them to various tests.

The sample container must be clean and should be rinsed out with water from the sampling line. Water must be allowed to run from the sampling line for sufficient time to ensure that any stagnant water in the line is not taken as the sample. The testing of the sample should be done as soon as the sample has cooled to room temperature and suspended solids have settled out.

The various impurities in the water which cause hardness and alkalinity are expressed as ppm of their calcium carbonate ($Ca\ CO_3$) equivalents. This equivalent refers to the molecular weight of the impurity compared to the molecular weight of $Ca\ CO_3$, and give a common basis for comparison of the impurities present.

The test commonly carried out on the feedwater and boiler water are briefly described in the following sections.

Hardness Test

Hardness of the water is due to impurities or salts such as those of calcium and magnesium which are dissolved in the water. These will cause scale in the boiler unless properly treated. To determine the amount of these mineral salts in the water, a sample of the water is subjected to a soap test. The impurities combine with the soap to form a scum and retard the formation of a lather. Therefore the amount of soap needed to combine with all the impurities will give an indication of the amount of impurities present.

The procedure in making the test is to obtain a sample of the water and filter it or let suspended solids settle out. Then add a measured amount of the filtered water to a clear glass bottle equipped with a glass or rubber stopper. Small measured amounts of a standard soap solution are added to the water with the bottle being shaken vigorously after each small addition of soap. When just enough soap is added to produce a lather that lasts five minutes all the mineral impurities are considered to have combined with the soap and the amount of soap used will indicate the hardness of the water in ppm of Ca CO_3.

Alkalinity Test

The alkalinity of the water may be due to hydroxides, carbonates and bicarbonates of calcium, sodium, magnesium, etc. The water can be tested to determine the amounts of these alkalies and the amounts are then expressed in ppm of Ca CO_3.

1. Phenolphthalein Alkalinity Test

This test indicates alkalinity due to carbonates and hydroxides dissolved in the water. It does not indicate alkalinity due to bicarbonates.

Phenolphthalein is a liquid which is used as an indicator of carbonate and hydroxide alkalinity. When a drop of this indicator is added to a sample of the water it will cause the water to become pink in color providing the water contains carbonates or hydroxides or both.

To conduct the test, a small amount of phenolphthalein is added to a measured sample of the water. If a pink color appears then sulphuric acid is added drop by drop to the water until the pink color just disappears. While this is being done the sample must be stirred constantly. The amount of acid required to make the pink color just disappear will indicate the amount of alkalinity known as phenolphthalein or "P" alkalinity and this is expressed in ppm of Ca CO_3. The sample is then put aside for the following test.

2. Total Alkalinity or Methyl Orange Test

This test is used to determine the amounts of all the dissolved materials which cause alkalinity of the water. The indicator used for this is methyl orange and it will give a yellow color to alkaline water.

To perform the test a small amount of methyl orange is added to the same sample as used in the previous test. If a yellow color is produced then this means that the sample is still alkaline due to bicarbonates present. Sulphuric acid is then added drop by drop until the yellow color turns to a salmon pink. This indicates that all the alkalinity has now been neutralized by the sulphuric acid and the total amount of acid used, namely that used for the methyl orange test plus that used for the phenolphthalein test will indicate the total alkalinity of the sample expressed in ppm of $CaCO_3$. The total alkalinity is also called methyl orange alkalinity or " M " alkalinity.

Dissolved Solids Test

To determine the amount of dissolved solids in the water the ability of the water to conduct an electric current is measured. The greater the amount of dissolved solids present in the water the greater will be this ability to conduct or the greater the conductance of the water.

To perform the test a sample of water is taken and a small amount of phenolphthalein is added. If a pink color appears then sulphuric acid is added drop by drop until only a faint tinge of pink remains. This is done to neutralize the hydroxide alkalinity as the hydroxide ion has a very high conductivity compared to ions of neutral salts and if not neutralized would render the conductance test inaccurate.

The conductance of the neutralized sample is now measured by means of an electrical instrument and the reading when multiplied by a conversion factor will give the dissolved solids in ppm.

pH Testing

The pH value of a water sample may be determined by the use of an electrical instrument known as a pH meter. Two electrodes are immersed in the sample and a voltage is supplied to the electrodes by means of a battery or a power pack. The voltage between the electrodes will vary according to the amount of the hydrogen ion concentration in the sample and this voltage is indicated on the pH meter which is calibrated to read in pH numbers.

Sodium Sulphite Test

In cases where sodium sulphite is fed to a boiler in order to prevent pitting due to dissolved oxygen, it is necessary to ascertain that sufficient amounts of sulphite are supplied. Usually if there is an excess of 20 ppm of sulphite maintained in the boiler water then the complete removal of any dissolved oxygen will be assured.

In determining the amount of excess sulphite in the boiler water, the following procedure is used:

> When obtaining the sample of boiler water, care should be taken to avoid contact of this water with the air. The sample should be cooled to room temperature but should not be filtered. A measured amount of the sample is then put in a porcelain dish and turned slightly acidic by the addition of sulphuric acid. A small amount of starch solution is added to the sample and then a potassium-iodide-iodate solution is added drop by drop until a permanent light blue color is attained. During this procedure the sample is stirred constantly. The amount of the potassium-iodide-iodate solution necessary to produce the permanent light blue color will indicate the ppm of excess sodium sulphite in the boiler water.

Phosphate Test

A common form of internal treatment for the prevention of scale in a boiler is the addition to the boiler water of sodium phosphate compounds. These will precipitate the scale forming materials as a sludge which may be blown off from the boiler through the blow-off line. In order to assure this precipitation of the scale forming materials, it is necessary to have an excess of phosphate in the boiler of from 30 to 60 ppm.

The following test is used to determine the amount of excess phosphate present:

> The sample of boiler water is thoroughly filtered. A measured amount is then poured into a mixing tube and molybdate reagent is added. The tube is then stoppered and vigorously shaken. The next step is to add dilute stannous reagent, which has been freshly prepared from concentrated stannous reagent and distilled water, to the mixture in the tube. This will produce a blue color and the lightness or darkness of the blue will indicate

the amount of phosphate in the water. The tube is compared with standard colored glass slides which are marked in ppm of phosphate.

The apparatus used in all of the foregoing tests should be thoroughly cleaned after using and then rinsed again with distilled water or with part of the water to be tested just before the testing is carried out. The testing room or laboratory should be equipped with a sink, hot and cold running water, electrical outlets, equipment cabinets and the necessary desks and tables.

- QUESTION SHEET -

POWER ENGINEERING

Third Class
Sect. 3, Lect. 12

1. Explain what is meant by impurities in water and what problems they can cause in a boiler.
2. What is caustic embrittlement? What factors are required to produce caustic embrittlement and how is embrittlement prevented?
3. Name the equipment available to treat the feedwater mechanically, chemically and thermally. What is the basic purpose of this equipment?
4. Sketch and describe the operation of a coagulator.
5. Make a sketch of a pressure filter. What is the purpose of back-washing this filter and how is a backwash operation carried out?
6. a) Explain the operation of a sodium zeolite softener.
   b) What are the purposes of backwashing, regenerating and rinsing such a softener and how are these processes carried out?
7. Sketch and describe the operation of a deaerator.
8. a) Why is it important that scale and mud are not deposited in a boiler?
   b) How are these deposits prevented from forming?
9. a) Compare intermittent blowdown with continuous blowdown.
   b) Make a drawing of a continuous blowdown system.
10. Describe briefly the following water tests:
    a) hardness
    b) P-alkalinity
    c) M-alkalinity
    d) sodium sulphite
    e) phosphate

12.2

FEEDWATER — WATER TREATMENTS

Goal:

The apprentice will be able to describe the basic feedwater treatments.

Performance Indicators:

1. Describe external treatments.
2. Describe internal treatments.
3. Describe sampling of boiler water and steam for testing.

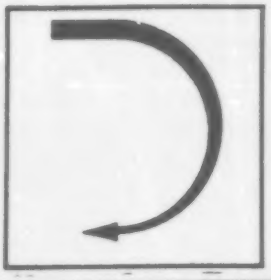
Study Guide

* Read the goal and performance indicators to find what is to be learned from package.
* Read the vocabulary list to find new words that will be used in package.
* Read the introduction and information sheets.
* Complete the job sheet.
* Complete self-assessment.
* Complete post-assessment.

Vocabulary

* Anion exchanger
* Caustic embrittlement
* Carryover prevention
* Chemical coagulation
* Continuous hot process softener
* Continuous sedimentation cold process softener
* Continuous sludge contact cold process softener
* Deaerators
* Deionization process
* Demineralized water
* Dissolved gases
* Dissolved solids
* Evaporation
* External treatment
* Filtration
* Foaming
* Hot lime--hot ion exchange softener
* Hot lime--phosphate softener
* Hydrazine
* Hydrogen ion exchanger
* Intermittent cold process softener
* Internal treatment
* pH control
* Priming
* Return line corrosion
* Reverse osmosis
* Sample cooler
* Sample testing
* Scale prevention
* Settling tanks
* Sodium hydroxide
* Sodium ion exchanger
* Sodium phosphate
* Spray type deaerator
* Steam sample
* Suspended matter
* Tray type deaerator
* Water sample
* Water softener
* Zeolite

Introduction



A steam plant is troubled with scale deposits and corrosion. Scale deposits reduce the ability of the unit to transfer heat. The level of scale formation is determined by the content and purity of the water used to make steam. High purity water used to make steam. High purity water becomes a major concern for the boiler operator.

This water is heated to form steam. As the water is transformed to steam, more water is fed into the boiler. The term feedwater is used to describe water that is fed into the boiler to become steam.

To avoid damage from feedwater, the water should be tested and the water treated according to the findings of the tests. Follow-up tests should be conducted to make sure that the treatment corrected the problem of water quality.

Information

Water Treatment

The purpose of feedwater treatment is to:

1. Remove salts that form scale.
2. Remove acid-forming materials.
3. Reduce dissolved oxygen content.
4. Regulate total dissolved solids content.

Water impurities that cause problems in feedwater are:

1. Suspended matter is material that does not dissolve in water and can be removed by filtering. Examples are organic material, clay, mud.

2. Dissolved solids such as calcium, magnesium and silica make compounds that form scale deposits. This problem requires treatment of the feedwater.

3. Dissolved gases such as oxygen and carbon dioxide corrode the boiler and piping. Mechanical aeration and chemical treatments are used to remove the dissolved gases from the feedwater.

The methods of treatment may be classified as:

1. External treatment of the water before it enters the boiler, i.e. evaporation, filters, deaerators.

2. Internal treatment by chemical means after it enters the boiler.

External Methods of Treatment

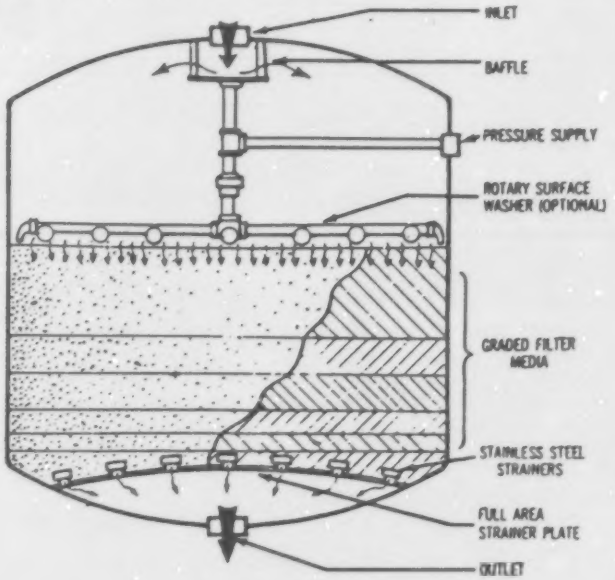
Several external methods of water treatment are used to purify the feedwater.

1. Settling tanks can be used to settle out suspended matter. Water is allowed to stand in the settling tank until suspended matter settles to the bottom and is drawn off. If the suspended matter is a fine particle such as clay, chemical coagulation can be used to increase the particle size and make it settle out. Aluminum compounds are common coagulants. Coagulation also removes some solids other than suspended matter.

2. Filtration involves passing raw water through filters of sand and gravel or other media. Filters trap most suspended materials.

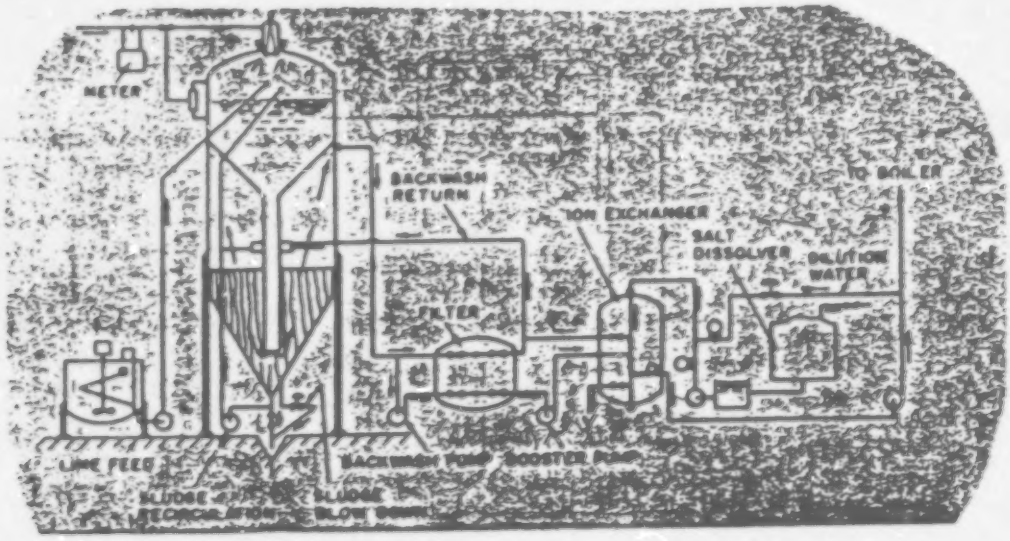
Information

Pressure filters will remove finer particles than a gravity filter unit. The filter media is graded in density and pressure is applied to push the water through the filter. A drawing of a pressure filter is shown.



3. Water softeners are used to remove scale forming dissolved solids from the feedwater. Lime (calcium hydroxide) and soda (sodium carbonate) precipitate the solids. A coagulant is then used to settle out the dissolved solids. Lime-soda softeners may be used as the intermittent cold process softeners for small plants; as continuous sedimentation cold process softeners that are continuously mixing lime and soda with water and the sedimentation process is on-going; continuous sludge contact cold process softener that mixes raw water with sludge and chemicals; and the continuous hot process. The continuous hot process softener is the most widely used. Chemicals and water are mixed and immediately heated to 100 C by steam. The solids precipitate and are removed by blow down. The hot lime-hot phosphate softener uses hot phosphate along with the hot lime softener. Almost all dissolved solids can be removed through this treatment. The hot lime softener can be combined with an ion exchanger to remove hardness and carbon dioxide from the water. A hot lime-hot ion exchange softener is shown on the next page.

Information



Hot Lime - Hot Ion Exchange

In the sodium ion exchanger, a sodium zeolite softener converts scale forming compounds to non-scale forming compounds. The zeolite changes calcium and magnesium to sodium compounds through ion exchange.

The hydrogen ion exchanger uses a hydrogen zeolite and converts calcium and magnesium into acids and then the acids are neutralized with sodium hydroxide. This softener avoids having carbon dioxide formed from the sodium bicarbonate that is the case with other softeners. The carbon dioxide causes erosion problems in boiler parts. Demineralized water uses a deionization process. First a hydrogen zeolite is used as a cation exchange to remove calcium and magnesium. Then an anion exchanger is used to remove sulphate, chloride and silica anions. A degasifier is used to remove carbon dioxide. This makes mineralized water almost as pure as distilled water.

Reverse osmosis is another system for cleaning up water. In osmosis, a dilute solution will pass through a membrane to a concentrated solution. However, if pressure is applied on the concentrated side, the fluid will pass to the dilute side in a reverse osmosis. If raw water is forced through a membrane, the impurities will be left behind. A reverse osmosis type softener is shown.

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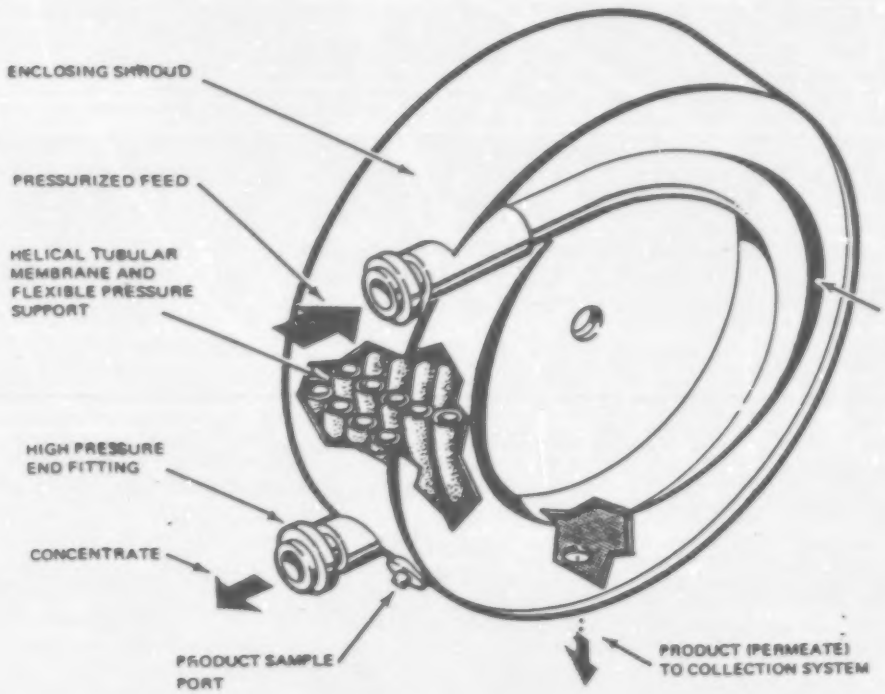
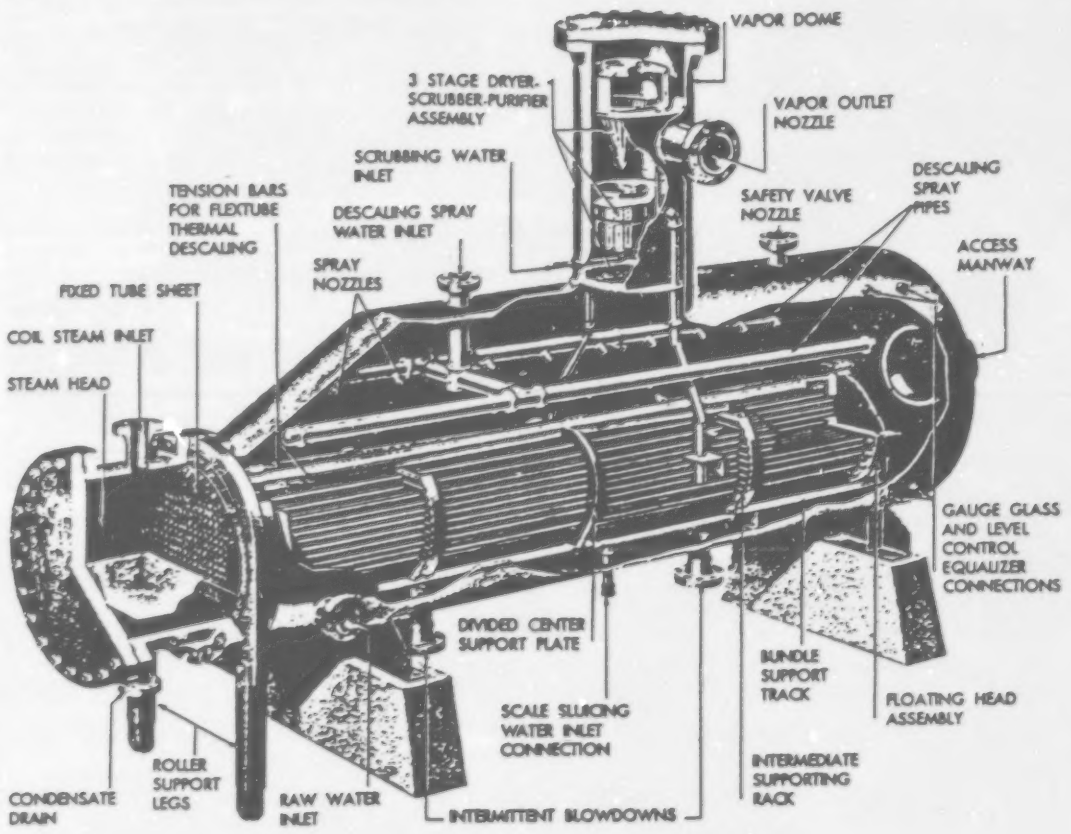
Information



4. Evaporation involves boiling water. The steam from boiling water is condensed and used as feedwater. Deaerators are used with evaporators so that both dissolved gases and minerals are removed from the feedwater. Water is usually softened before evaporation to avoid scale formations in the evaporator. A typical evaporator is shown on the following page.

Information



5. Deaeration is used to remove dissolved gases from water. Oxygen and carbon dioxide cause corrosion in boilers. It is wise to remove as much of the dissolved gases as possible through deaeration. Mechanical deaeration involves heating the water to the boiling point and pushing the gases into the atmosphere. During this process the water is scrubbed with steam to remove the gases from the water. Deaerators consist of four sections. They are either of a spray type or tray type. In the spray type water is sprayed into the first section where it is heated; moved through the scrubbing section; moved into storage section as deaerated water; and the gases move to the last section and then outside. The tray type deaerator is very much like the spray type except that the water trickles down over trays instead of being broken up by spray nozzles.

Information

Internal Methods of Treatment

Internal treatment is conducted after the water has entered the boiler. It may be used as the only treatment in some low pressure boilers or in addition to external treatments. Some of those internal treatments are:

1. pH Control — prevents acids in boiler water from corroding the metal. The pH must be kept high (10.5) by adding a base solution. Sodium hydroxide has been used in years past but is now found to cause a problem called caustic embrittlement. To avoid this problem, operaters should use sodium phosphates for raising the pH level of boiler water.

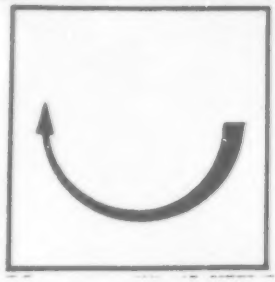
2. Scale prevention treatments involve precipitating calcium and magnesium salts and removing them as sludge during blow-off. The sodium phosphates are the most suitable chemical for precipitation of salts that later become scale.

3. Oxygen scavenging. The feedwater brings undissolved oxygen into the boiler. This oxygen will cause corrosion of the boiler, feedwater lines, heaters and economizer. Mechanical deaeration should be practiced on all feedwater. In addition, this should be followed by oxygen scavenging or chemical deaeration to remove the remaining oxygen. Sodium sulphite is the chemical to be used in scavenging. With some high pressure boilers hydrazine, a strong alkali, is used for scavenging oxygen.

4. Carryover prevention involves steps to assure that boiler water solids do not leave in the steam. A previous package discussed priming which involves carryover of water in the steam. Foaming is a condition where bubbles form in the boiler. These bubbles cause water to be carried over in the steam. There are many causes for water carryover including chemical and mechanical reasons. Blow-down reduces the amounts of suspended solids and prevents carryover. Such things as oil in the boiler can cause foaming and carryover. There is no internal treatment for oil in the boiler. Many new anti-foam agents are available to help control carryover by foaming.

5. Return line corrosion is caused by carbon dioxide and oxygen in the condensate solution. Mechanical and chemical aeration can prevent problems with oxygen. Carbon dioxide can be controlled by the use of ammonia, neutralizing amines and filming amines. Ammonia is corrosive to copper and zinc bearing metals.

Information



Sampling Boiler Water and Steam

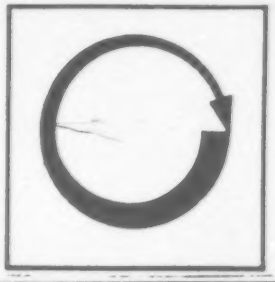
The operator must be able to collect samples for testing. That is the only way to determine the quality and purity of boiler water and steam. The sample must be representative of the total water and steam capacity.

1. Water samples should be collected from an internal pipe or from the continuous blow down pipe. The samples should be cooled to room temperature in a sample cooler.

2. Steam samples are taken from the drum by sampling lines. It is condensed and cooled in a sample cooler.

3. Sample testing must be carefully done to avoid contamination of samples. The test instructions must be followed closely if good results are expected.

Assignment



* Read pages 1 - 33 in the supplementary reference.
* Complete job sheet.
* Complete self-assessment and check answers.
* Complete post-assessment and ask the instructor to check your answers.

Job Sheet

ASSIST OPERATOR IN COLLECTING WATER AND STEAM SAMPLES

* Ask a boiler operator if you can observe the techniques for collecting and preparing samples of water and steam for testing.
* Assist operator in collecting samples.
* Record the steps in collection procedure.
* Record steps in sample preparation such as cooling.

Self Assessment

Match the following terms and phrases.

____	1. Dissolved gases	A.	Removes scale forming dissolved solids from water.
____	2. Dissolved solids	B.	Requires water to pass through a membrane under pressure.
____	3. Suspended matter	C.	Increases particle size so that it will settle out.
____	4. Chemical coagulation	D.	Make compounds that cause scale.
____	5. Water softeners	E.	Involves boiling water into steam and condensing it.
____	6. Demineralized water	F.	Cause corrosion in boiler and piping.
____	7. Zeolite	G.	Does not dissolve in water.
____	8. Evaporation	H.	Used to remove dissolved gases form feedwater.
____	9. Deaeration	I.	Requires cation exchanger, anion exchanger and degasifier to manufacture it.
____	10. Reverse osmosis	J.	Changes calcium and magnesium compounds to sodium compounds.

Self Assessment Answers

F 1.

D 2.

G 3.

C 4.

A 5.

I 6.

J 7.

E 8.

H 9.

B 10.

Post Assessment

Match the following terms and phrases.

____	1. Spray type	A.	Removal of oxygen by chemical deaeration.
____	2. Sodium hydroxide	B.	Removes scale forming elements such as calcium, magnesium and silica.
____	3. Sodium phosphate	C.	Used to remove suspended matter from water.
____	4. Oxygen scavenging	D.	Avoids caustic embrittlement.
____	5. Foaming	E.	Type of deaerator.
____	6. Sodium sulphite	F.	Chemical used in oxygen scavenging.
____	7. Ammonia	G.	Causes caustic embrittlement.
____	8. Water softener	H.	Caused by carbon dioxide and oxygen in the condensate solution.
____	9. Settling tank	I.	A type of water carryover into steam.
____	10. Return line corrosion	J.	Corrosive to copper and zinc bearing metal.

Instructor Post Assessment Answers

E 1.

G 2.

D 3.

A 4.

I 5.

F 6.

J 7.

B 8.

C 9.

H 10.

Supplementary References

* Correspondence Course. Lecture 12, Section 2, First Class. Steam Generation. Southern Alberta Institute of Technology. Calgary, Alberta, Canada.

SOUTHERN ALBERTA INSTITUTE OF TECHNOLOGY
CALGARY, ALBERTA

Correspondence Courses
Power Engineering

SECTION 2

First Class
Lecture 12

STEAM GENERATION

WATER TREATMENT

Impurities are always present in any water supply and these impurities must be determined by analysis and then controlled by water treatment. Water treatment involves the removal of undesirable impurities and, often, the addition of desirable substances such as corrosion inhibitors or precipitating or coagulating agents.

The impurities that may be present in a water supply can be classified into three main groups; suspended matter, dissolved solids, and dissolved gases.

Suspended matter consists of materials which do not dissolve in the water and which therefore can be removed by filtration and/or subsidence. Examples are mud, sand, clay, and organic material such as sewage, algae and vegetable matter.

The dissolved solids which cause the most trouble in a boiler are calcium, magnesium, and silica. Compounds of these elements form deposits which inhibit heat transfer and which may even clog fluid transmission systems. As these compounds are dissolved in the water they cannot be removed by filtration or subsidence, instead some other type of treatment must be employed, such as softening, demineralization, evaporation or internal chemical treatment.

Dissolved gases commonly found in water are oxygen and carbon dioxide and if not removed will cause corrosion of boiler and piping. Treatment for dissolved gases usually consists of mechanical deaeration together with chemical treatment.

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METHODS OF TREATMENT

There are two main classifications of water treatment, namely, external treatment and internal treatment.

External treatment refers to the treating of the water before it enters the boiler and includes the use of filters, settling tanks, water softeners, demineralizers, reverse-osmosis installations, deaerators and evaporators.

Internal treatment refers to the treating of the water within the boiler by chemical means.

External Methods

1. Settling and Coagulation

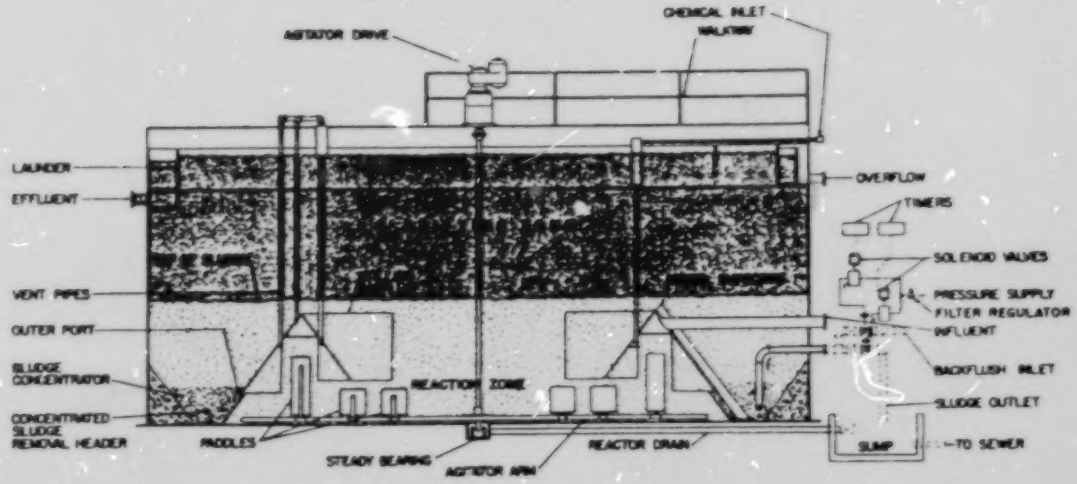
Settling or subsidence may be used to remove suspended matter from water. A simple tank may be used into which the water is introduced and allowed to stand until the sediment has settled. The clarified water is then decanted off and the sediment removed from the bottom of the tank which is then refilled for another cycle.

A continuous method of subsidence consists of passing the water through a basin or pond of such size and design that the velocity of the flowing water is low enough to let sand and silt settle before the water leaves the pond.

If the water contains suspended matter of low specific gravity or of fine particle size then chemical coagulation is necessary to increase the size of the particles so that they will settle out more readily.

The chemicals used for coagulation have the effect of neutralizing the negatively charged surfaces of the suspended particles thus allowing them to attract each other and form larger particles. The coagulant chemicals also form insoluble floc particles which tend to enmesh the very small particles.

Aluminum compounds, especially alum, $Al_2 (SO_4)_3 \cdot 18 H_2O$, and sodium aluminate, $Na_2 Al_2 O_4$, are the most widely used coagulants. They produce a tough, heavy aluminum-hydroxide floc which entraps the suspended solids. This floc is insoluble as long as the pH of the water remains between 5.7 and 7.5. It will dissolve, however, if the pH is below 5.7 or above 7.5. Therefore the pH must be properly adjusted and closely controlled and this is done by adding an acid or an alkali to maintain correct pH during coagulation.



Solids Contact Reactor
(Crane Cochrane)

Fig. 1

The solids contact reactor shown in Fig. 1 produces clarification of the water by means of coagulation. The coagulation chemicals are admitted through the chemical inlet shown in the sketch. If desired, other chemicals in addition to the coagulants may be used to reduce alkalinity, to soften the water, and to remove silica from the water.

The raw water and the chemicals are introduced adjacent to each other near the bottom of the reactor. They are thoroughly mixed together and a slurry of floc is produced which is kept in suspension by the agitator. The incoming water is then directed to the centre of the reactor where it rises into the clarifying zone. As the water rises through the floc, the suspended particles are removed and the clarified water leaves via the effluent outlet. The settled out solids collect in the sludge concentrator and are removed periodically to waste. The opening of the sludge outlet valve is initiated by a raw water flowmeter and closed by a timer. The sludge removal lines are back-flushed before the sludge outlet valve opens to avoid clogging of the lines.

(PE1-2-12-3)

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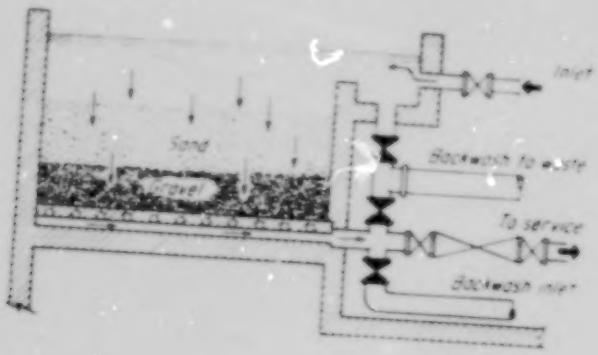
2. Filtration

Essentially, a filter consists of a bed of porous material through which the water is passed either by gravity or under pressure. Any suspended matter in the water is trapped by the porous material thus clarifying the water.

Filters are frequently used in conjunction with settling or sedimentation as the final step in clarification. Alternately, they may be used as the only clarification step, in which case a coagulant is usually fed to the filter to aid in the trapping of solids.

The flow through a gravity filter is produced by gravity and this type usually uses sand or coal as the filter medium.



Gravity Filter

Fig. 2

A sand gravity filter appears in Fig. 2. In operation, most of the solids will be trapped in the top 100 mm of the filter medium. When this section becomes clogged, the bed must be backwashed to remove the trapped solids and restore the unit's filtering efficiency.

Pressure filters are more widely used in industry than are gravity units as they can be installed in piping systems under pressure.

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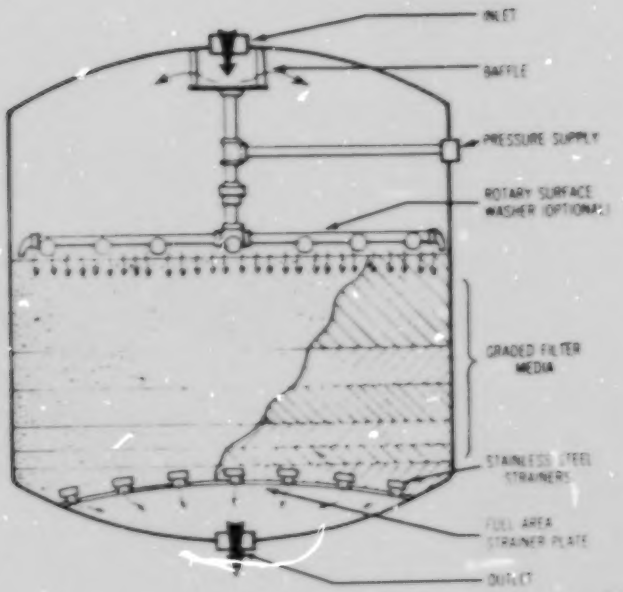

Pressure Filter

Fig. 3

A pressure filter is shown in Fig. 3. The shell is of steel and contains a bed of anthracite which is supported on a strainer plate. The water to be filtered is pumped under pressure through the filter, entering at the top and passing down through the filter bed and through stainless steel strainers to the outlet at the bottom.

During the backwashing period, a rotary surface washer may be used to loosen material from the surface of the bed.

For removal of very fine particles (less than 1 micron), precoat pressure filters are used. These filters use a porous septum such as wire screen or cloth in the form of leaves or in the form of tubes. These tubes or leaves are coated with a filter cake of cellulose powder or, if silica can be tolerated, the filter cake consists of diatomaceous earth.

When the precoat filter becomes dirty, as evidenced by high back pressure, the filter cake and the particles imbedded in the filter cake must be removed from the filter elements. With the leaf type the filter cake is peeled off manually while the tubular type is backwashed. A new precoat of filter cake is then added in the form of a slurry and the filter is returned to service.

The precoat filter does not require coagulants with their attendant pH control.

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3. Lime-Soda Softeners

Lime-soda softening involves the removal from the water of the scale forming dissolved solids such as calcium and magnesium salts. Calcium hydroxide (lime) and sodium carbonate (soda) are used to cause the scale forming materials to precipitate and a coagulant is used to aid in the settling out of the precipitated material.

The lime, $Ca(OH)_2$, is used to remove the bicarbonates of magnesium and calcium by converting them to insoluble carbonates which precipitate. The following chemical reactions illustrate this.

1. Calcium bicarbonate + Calcium hydroxide ⟶ Calcium carbonate + Water

$$Ca(HCO_3)_2 + Ca(OH)_2 \longrightarrow 2\,CaCO_3 + 2\,H_2O$$

2. Magnesium bicarbonate + Calcium hydroxide ⟶ Magnesium hydroxide + Calcium carbonate + Water

$$Mg(HCO_3)_2 + 2\,Ca(OH)_2 \longrightarrow Mg(OH)_2 + 2\,CaCO_3 + 2\,H_2O$$

Other scale forming compounds such as magnesium sulphate $MgSO_4$; magnesium chloride $MgCl_2$, calcium sulphate $CaSO_4$, and calcium chloride $CaCl_2$ are also removed by the lime-soda process by reacting with the calcium hydroxide or the sodium carbonate as shown below.

3. Magnesium sulphate + Calcium hydroxide ⟶ Magnesium hydroxide + Calcium sulphate

$$MgSO_4 + Ca(OH)_2 \longrightarrow Mg(OH)_2 + CaSO_4$$

In the above reaction the $Mg(OH)_2$ is insoluble and will precipitate but the $CaSO_4$ is soluble and must react with sodium carbonate to form insoluble calcium carbonate as follows.

4. Calcium sulphate + Sodium Carbonate ⟶ Calcium carbonate + Sodium sulphate

$$CaSO_4 + Na_2CO_3 \longrightarrow CaCO_3 + Na_2SO_4$$

The Na_2SO_4 formed above is extremely soluble and will not form scale in the boiler.

(PE1-2-12-6)

5. Magnesium chloride + Calcium hydroxide ⟶ Magnesium hydroxide + Calcium chloride

$Mg\,Cl_2 + Ca\,(OH)_2 \longrightarrow Mg\,(OH)_2 + Ca\,Cl_2$

In the above reaction the $Ca\,Cl_2$ is soluble and must be treated with sodium carbonate to form insoluble calcium carbonate which will precipitate.

6. Calcium chloride + Sodium carbonate ⟶ Calcium carbonate + Sodium chloride

$Ca\,Cl_2 + Na_2\,CO_3 \longrightarrow Ca\,CO_3 + 2\,Na\,Cl$

The Na Cl formed above is extremely soluble and will not form scale in the boiler.

In addition to the removal of the calcium and magnesium scale forming compounds, the lime-soda process will also reduce the silica content of the water. This is because the silica will react with the $Mg\,(OH)_2$ to form an insoluble complex silicon-magnesium compound. To facilitate this reaction, additional magnesium oxide is usually supplied to softener together with the lime and soda.

Lime-soda softeners may be of four different basic types: intermittent cold process; continuous sedimentation cold process; continuous sludge contact cold process; and continuous hot process.

Intermittent cold process softeners are used for small plants and use two tanks with one tank supplying soft water while the other tank is being cleaned, refilled and put back into service. This system has a low initial cost but has the disadvantage of a long sedimentation period and the need for considerable manual operation and attendance.

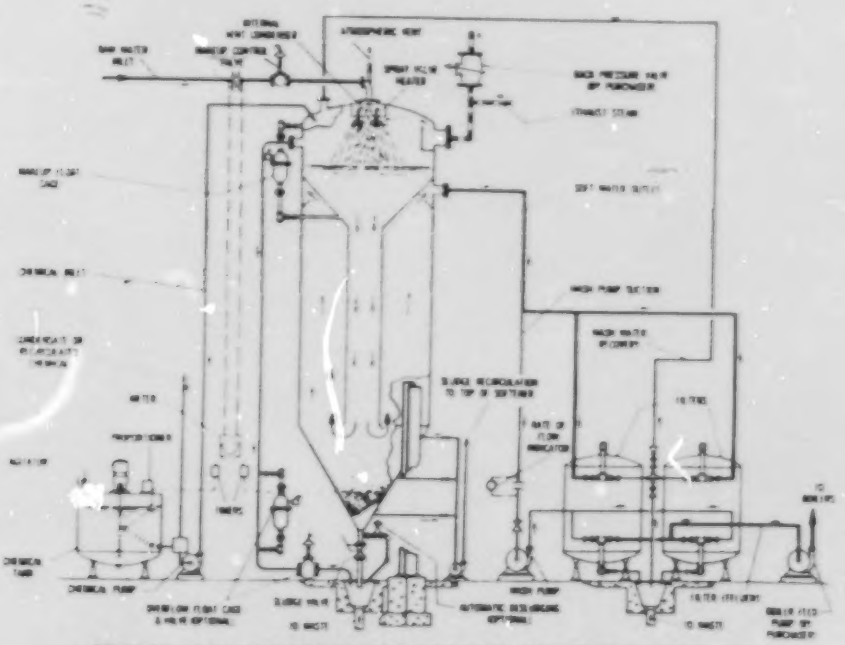
The continuous sedimentation cold process softener is much like a coagulation and sedimentation basin where the raw water is continuously mixed with lime, soda and coagulant in a small chamber of the basin. The mixture then flows to a flocculator section and then to a sedimentation section where the sludge is deposited over a four hour period and the water then drawn off. It has the advantages of low maintenance and operating costs and the disadvantages of high construction cost and large space requirements.

The continuous sludge contact cold process softener uses a reactor such as that shown in Fig. 1. The raw water is mixed with previously precipitated sludge as well as the treatment chemicals. The calcium and magnesium are precipitated and deposit in the sludge bed and the effluent is filtered as it passes through the bed.

The continuous hot process is the lime-soda softener most often used for boiler feedwater. The process is designed to operate at 100°C or above using live or exhaust steam as a heat source. Chemicals are fed into the softener in proportion to the amount of raw water entering. The raw water is heated by steam as it enters and the higher temperatures of this process make chemical reactions almost instantaneous and sedimentation occurs rapidly.

Blowdown is used to remove the precipitated material and the soft water leaving is passed through a pressure filter for final clarification. The process thus combines calcium and magnesium salts removal, silica removal, deaeration and filtration.

Fig. 4 illustrates the arrangement of a hot process lime-soda softener with filters.



GRAVER FLOW DIAGRAM—HOT PROCESS SOFTENER—TYPE "F"

Graver Water Conditioning Co.

Fig. 4

(PE1-2-12-8)

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In Fig. 4 the raw water, chemicals, and steam all enter near the top of the softener. The sludge which forms at the bottom is recirculated by means of a pump to the top of the tank. This recirculation aids in the formation of the precipitates and adds to the economy of the operation.

The water leaving the softener passes through pressure filters for final clarification. A backwash pump is provided by means of which the filters may be backwashed using water from the softener which is subsequently recovered by returning it to the softener.

Because the water is heated to 100°C or above in the hot process, deaeration is achieved with dissolved gases and some steam passing off from the water. The steam is condensed in the vent condenser section while the gases, usually oxygen and carbon dioxide, escape through the vent.

Although the hot process lime-soda softener is much more efficient than the cold process type, it can only reduce hardness to approximately 10 to 30 ppm. If further reduction of hardness is required then some other form of softening must be used in addition to the lime-soda process.

For example, the hot lime-soda process may be followed by a hot phosphate process or by an ion exchange process. Of the latter two methods, the ion exchange has the most advantages and is more commonly used than the hot phosphate.

Hot Lime-Hot Phosphate

By using a hot phosphate softener in conjunction with a hot lime softener, water of close to zero hardness can be produced.

The chemicals used in the hot phosphate process are sodium hydroxide, Na OH, and trisodium phosphate. The calcium hardness is precipitated as tricalcium phosphate which is even more insoluble than the calcium carbonate precipitated in the lime-soda process. The magnesium hardness is precipitated as magnesium hydroxide. The softening reactions are as follows:

1. Calcium bicarbonate + Sodium hydroxide ⟶ Calcium carbonate + Sodium Carbonate + Water

$$3\,Ca(HCO_3)_2 + 6\,NaOH \longrightarrow 3\,CaCO_3 + 3\,Na_2CO_3 + 6\,H_2O$$

2. Calcium carbonate + Trisodium phosphate ⟶ Tricalcium phosphate + Sodium carbonate

$3\ Ca\ CO_3 + 2\ Na_3\ PO_4 \longrightarrow Ca_3\ (PO_4)_2 + 3\ Na_2\ CO_3$

3. Magnesium bicarbonate + Sodium hydroxide ⟶ Magnesium hydroxide + Sodium carbonate + Water

$Mg\ (HCO_3)_2 + 4\ Na\ OH \longrightarrow Mg\ (OH)_2 + 2\ Na_2CO_3 + 2\ H_2O$

4. Calcium sulphate + Trisodium phosphate ⟶ Tricalcium phosphate + Sodium sulphate

$3\ Ca\ SO_4 + 2\ Na_3\ PO_4 \longrightarrow Ca_3(PO_4)_2 + 3\ Na_2\ SO_4$

5. Magnesium chloride + Sodium hydroxide ⟶ Magnesium hydroxide + Sodium chloride

$Mg\ Cl_2 + 2\ Na\ OH \longrightarrow Mg\ (OH)_2 + 2\ Na\ Cl$

As with the lime-soda process, the hot phosphate process will remove silica from the water by means of the $Mg\ (OH)_2$.

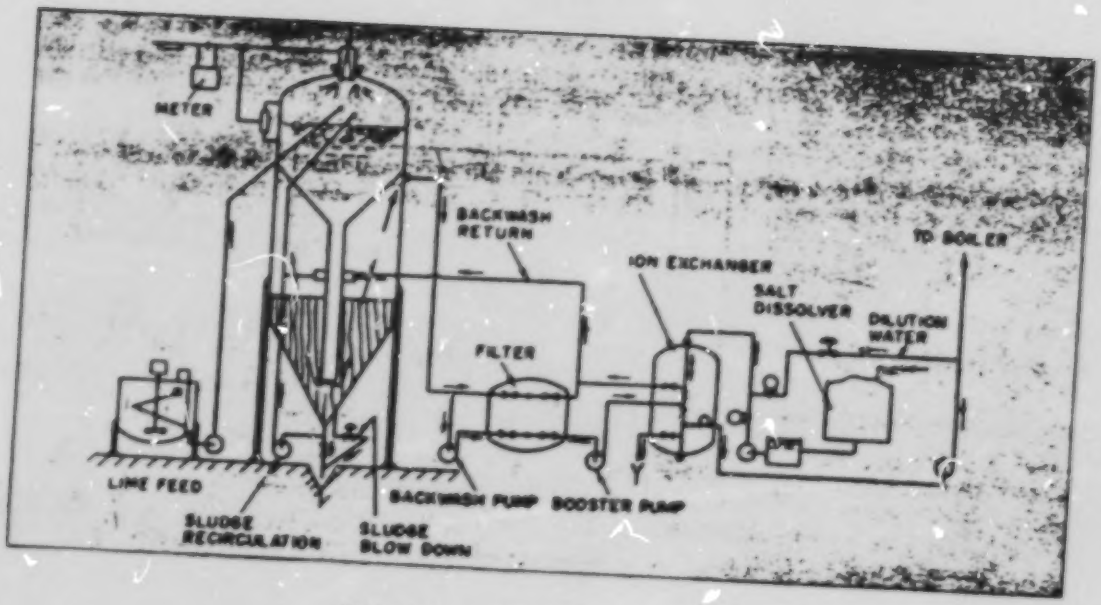
Hot Lime - Hot Ion Exchange

Instead of using a hot phosphate process after a hot lime softener, an ion exchanger can be used after the hot lime softener giving more complete hardness removal and less carbon dioxide content of steam produced in the boiler.

In this arrangement only lime is used in the hot process unit instead of using both lime and soda. The hardness normally removed by the soda is removed by the ion exchanger. By not using the soda the alkalinity of the effluent is reduced.

Fig. 5 shows an arrangement of a hot lime-hot ion exchange softener.

The chemical reactions taking place in an ion exchanger will be described in the next sections.



Hot Lime - Hot Ion Exchange

Fig. 5

4. Sodium Ion Exchanger

The sodium ion exchanger, usually called the sodium zeolite softener, uses the principle of ion exchange to convert scale forming compounds in the water to non-scale forming compounds. The softener contains a granular material called zeolite which has the ability to convert scale forming calcium and magnesium compounds to non-scale forming sodium compounds. This conversion is done by means of ion exchange. The zeolite removes the Ca and Mg cations from the water and replaces them with Na cations. The Ca and Mg cations are held by the zeolite which has given up Na cations in exchange for them.

When the zeolite material has given up all its Na cations, it has to be regenerated before it can resume the softening process. The regeneration is done by removing the zeolite softener from service and filling it with a solution of brine (Na Cl). The zeolite then absorbs the Na cations from the brine and discards the Ca and Mg cations to the brine. The brine, now containing the Ca and Mg cations is then flushed to sewer and the zeolite bed rinsed out with water and the softener is then returned to service.

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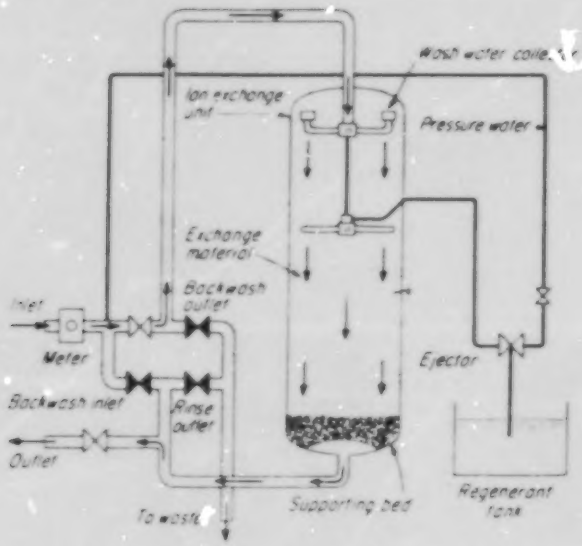
An arrangement of an ion exchange unit appears in Fig. 6.



Ion Exchange Arrangement

Fig. 6

5. Hydrogen Ion Exchanger

In the sodium cation exchange softener, explained in the previous section, the salts of calcium and magnesium were replaced with salts of sodium. While this method does get rid of the scale-forming calcium and magnesium, it does not reduce the total amount of salts dissolved in the water as the sodium salts take the place of the calcium and magnesium salts. One of these sodium salts, sodium bicarbonate, will decompose in the boiler into sodium carbonate, sodium hydroxide and carbon dioxide. The sodium hydroxide may cause embrittlement of the boiler metal and the carbon dioxide will be carried over with the steam and form carbonic acid in the return lines which results in corrosion. Sodium bicarbonate will also tend to cause the water in the boiler to foam.

If instead of a sodium zeolite softener, a hydrogen zeolite softener is used, then the scale forming salts will be removed without the formation of sodium bicarbonate. Hydrogen zeolite has the ability to remove calcium, magnesium and sodium cations from the mineral salts and replace them with hydrogen ions. As a result the mineral salts are converted to acids. These acids are subsequently neutralized by the use of an alkali or base such as caustic soda Na OH, or in some cases the acid-containing water from the hydrogen zeolite softener is mixed with the water from a sodium zeolite softener and this will also result in the neutralization of the acids.

(PE1-2-12-12)

Regeneration of the hydrogen zeolite is accomplished by the use of an acid solution which restores hydrogen ions to the zeolite and removes the calcium, magnesium and sodium cations from the zeolite.

The chemical reactions taking place in the hydrogen exchanger are as follows:

1. Calcium bicarbonate + Hydrogen zeolite ⟶ Calcium zeolite + Carbonic acid

$$Ca(HCO_3)_2 + H_2Z \longrightarrow CaZ + 2\,H_2CO_3$$

The reactions for magnesium and sodium bicarbonates are the same as the above.

2. Calcium sulphate + Hydrogen zeolite ⟶ Calcium zeolite + Sulphuric acid

$$CaSO_4 + H_2Z \longrightarrow CaZ + H_2SO_4$$

The reactions for sodium and magnesium sulphate are the same as the above.

3. Calcium chloride + Hydrogen zeolite ⟶ Calcium zeolite + Hydrochloric acid

$$CaCl_2 + H_2Z \longrightarrow CaZ + 2\,HCl$$

The reactions for sodium and magnesium chloride are the same as above.

4. Calcium nitrate + Hydrogen zeolite ⟶ Calcium zeolite + Nitric acid

$$Ca(NO_3)_2 + H_2Z \longrightarrow CaZ + 2\,HNO_3$$

The reactions for sodium and magnesium nitrate are the same as above.

When the hydrogen zeolite becomes exhausted it is backwashed and regenerated with acid, usually sulphuric, and the following equation represents the reaction:

Calcium zeolite	+	Sulphuric acid	⟶	Hydrogen zeolite	+	Calcium sulphate
$Ca\ Z$	+	$H_2\ SO_4$	⟶	$H_2\ Z$	+	$Ca\ SO_4$

The reactions involving Mg Z and Na_2 Z are similar to the above.

As indicated in equations 1 to 4 inclusive, the effluent from the zeolite exchanger contains various acids. A degasifier can be used to remove the carbonic acid from the effluent but the other acids, sulphuric, hydrochloric and nitric cannot be removed in this way and must be neutralized.

Neutralization of the acid effluent may be accomplished by operating a sodium zeolite unit in parallel with the hydrogen zeolite unit so as to obtain the desired pH in the mixed effluent.

Neutralization may also be accomplished by adding caustic soda or soda ash to the effluent.

A third method of neutralization involves the addition of raw unsoftened water to the hydrogen zeolite effluent. This method is possible if the raw water is of low total hardness and has high alkalinity.

The neutralization of the acid effluent by means of caustic soda is represented by the following equation.

Sulphuric acid	+	Caustic soda	⟶	Sodium sulphate	+	Water
$H_2\ SO_4$	+	$2\ Na\ OH$	⟶	$Na_2\ SO_4$	+	$2\ H_2O$

6. Demineralization

An advantage of the hydrogen zeolite process over the sodium zeolite process is that the hydrogen zeolite removed the sodium bicarbonate and thus reduced the dissolved solids content of the water. The acids in the effluent from the hydrogen zeolite unit, such as sulphuric and hydrochloric, were then neutralized. However when these acids were neutralized, the anions of these acids,

such as SO_4 and Cl, combined with the sodium from the neutralizing base NaOH and formed sodium sulphate and sodium chloride. While these sodium salts do not tend to form scale, they may cause foaming in the boiler and require excessive blowdown. In addition to this disadvantage, the hydrogen zeolite unit will not remove any silica present in the water.

If it is desired to remove all the mineral salts from the water, a process known as demineralization or deionization is used. This involves using a hydrogen zeolite cation exchanger to remove the sodium, magnesium and calcium cations and then using an anion exchanger to remove the sulphate, chloride and silica anions. In addition, a degasifier is used to remove any carbon dioxide present. The effluent from the demineralizing process is water that is free from all mineral impurities and is equal in quality to distilled water.

The hydrogen zeolite cation exchanger has already been described in the previous section.

The anion exchanger contains a hydroxide resin material which has the ability to remove the anions of the acids contained in the effluent from the cation exchanger. This anion exchange material is regenerated with sodium hyroxide when it becomes exhausted.

The anion exchanger hydroxide resin can be represented by the formula $E(OH)_2$ and the chemical reactions of this resin with the acid effluent from the cation exchanger are as follows:

5. Sulphuric acid + Resin ⟶ Resin sulphate + Water

$$H_2SO_4 + E(OH)_2 \longrightarrow E SO_4 + 2 H_2O$$

6. Hydrochloric acid + Resin ⟶ Resin chloride + Water

$$2 H Cl + E(OH)_2 \longrightarrow E Cl_2 + 2 H_2O$$

7. Nitric acid + Resin ⟶ Resin nitrate + Water

$$2 H NO_3 + E(OH)_2 \longrightarrow E(NO_3)_2 + 2 H_2O$$

(PE1-2-12-15)

If the raw water entering the cation exchanger contains silica then the effluent will contain silicic acid which is removed in the anion exchanger as follows:

8. Silicic acid + Resin ⟶ Resin silicate + Water

$$2\,H\,Si\,O_3 + E\,(OH)_2 \longrightarrow E\,(Si\,O_3)_2 + 2\,H_2O$$

When the anion exchange resin is exhausted it is regenerated with caustic soda as follows:

Resin sulphate + Caustic soda ⟶ Resin + Sodium sulphate

$$E\,SO_4 + 2\,Na\,OH \longrightarrow E\,(OH)_2 + Na_2\,SO_4$$

Similar equations are involved in the reaction of caustic soda with resin chloride, resin nitrate and resin silicate.

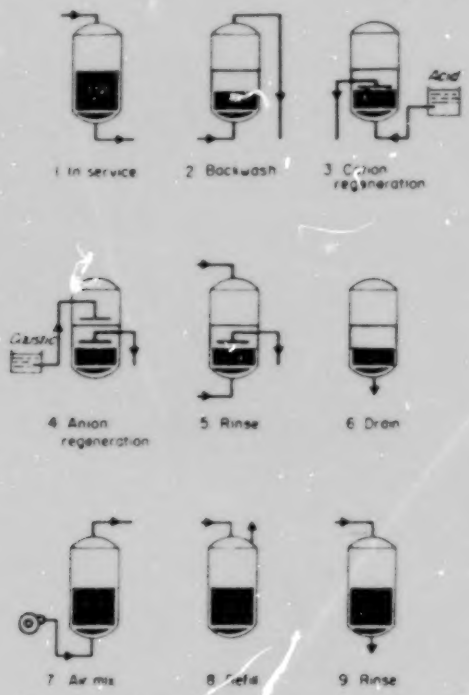
Various arrangements may be used for demineralizing equipment and these include the two-bed system, the mixed-bed system, and the continuous ion exchange system.

The two-bed system has cation and anion exchange materials in separate units, usually a hydrogen cation exchanger followed by an anion exchanger often with a degasifier between them.

The mixed-bed system features the cation and anion resins contained in the same tank or shell. When in operation the cation and anion resins are mixed together intimately. Before regeneration, the unit is backwashed to clean the beds and to separate the resins. During the washing the lighter anion resin rises to the top while the heavier cation resin settles to the bottom. The cation resin is then regenerated with acid which is introduced at the bottom of the unit and discharged from the unit at the interface of the resins. The anion resin is regenerated with a caustic solution brought in at the top and discharged at the resin interface. The unit is then rinsed and partly drained and the two resins are then mixed by means of air stream forced through the bed. The unit is then filled and rinsed again before its return to service.

(PE1-2-12-16)

Fig. 7 illustrates the regeneration steps.



Mixed Bed Regeneration

Fig. 7

The continuous ion exchange system is usually arranged in mixed-bed form although separate beds may also be used. The system provides continuous ion exchange because the total amount of resin is not allowed to become exhausted. Instead, the portion of the resin located at the raw water inlet will become exhausted first, and is withdrawn from the unit. At the same time, fresh regenerated resin is introduced at the other end of the bed. The withdrawn exhausted resin is regenerated in a separate vessel and then returned to service as required.

Fig. 8 shows a continuous ion exchange, mixed-bed demineralizer.

Referring to Fig. 8, when a predetermined volume of water has passed through the mixed-bed tank, the tank is briefly (30 - 90 seconds) removed from service for resin removal. During this time, exhausted resin is removed from the bottom of the unit and an equal amount of freshly regenerated resin is admitted at the top.

(PE1-2-12-17)

The exhausted resin then enters the separation column where the lighter anion resin rises to the top and the more dense cation resin settles to the bottom. The two resins then enter their respective desorption towers where they undergo regeneration and rinsing. The regenerated resins then travel to their respective metering hoppers located above the mixing hopper of the mixed-bed adsorption tank.

Mixed-Bed Continuous Ion Exchange

Fig. 8

The claimed advantages of the continuous ion mixed bed system compared to the conventional fixed-two-bed system where regeneration of the resin is carried out in place are: lower initial and installed cost, lower operating cost due to high chemical efficiency, less space required, operation is fully automatic, and maintenance requirements are low.

There is, however, another type of continuous ion exchange system which does use conventional fixed beds. This arrangement requires three identical ion exchange units which are operated in sequence. Unit A is in service, Unit B on standby and Unit C is being regenerated. When Unit A is almost exhausted, its effluent is then directed to Unit B, the standby unit. When Unit A is completely exhausted, its regeneration is begun and Unit C, which is now completely regenerated is on standby, while Unit B is in service.

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7. Reverse Osmosis

When two solutions, one dilute and one concentrated, are separated by a semi-permeable membrane, the solvent (water) from the dilute solution will diffuse through the membrane into the concentrated solution. This phenomenon is known as osmosis.

If, however, under the above conditions pressure is applied to the concentrated solution, the solvent (water) will diffuse through the membrane into the dilute solution and this phenomenon is known as reverse osmosis.

The reverse osmosis principle can be applied for water treatment because, as the water diffuses through the membrane, the impurities including the dissolved solids contained by the water are left behind and the diffused water is therefore of high purity.

The principles of osmosis and reverse osmosis are shown in Fig. 9.

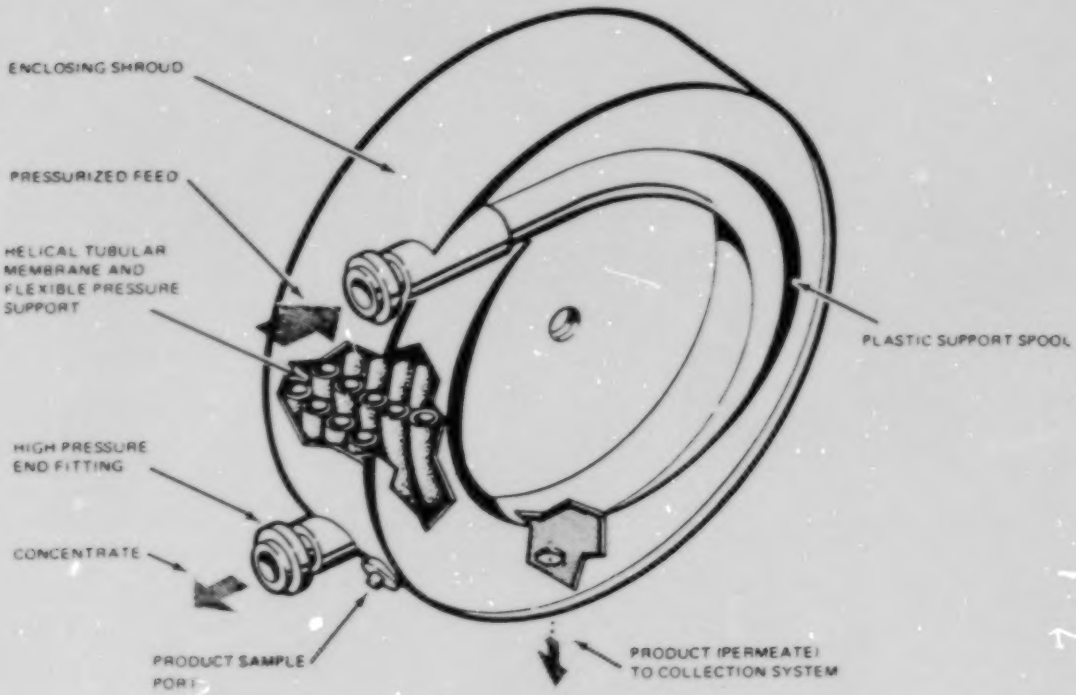
Osmosis and Reverse Osmosis

Fig. 9

The actual reverse osmosis water treatment plant is made up of a number of membrane modules through which the water passes in parallel. The modules are usually in the form of tubes lined with the membrane and Fig. 10 shows a module having a tubular membrane wound onto a support spool in a multiple layer helical coil.

(PE1-2-12-19)

In Fig. 10 the raw water is forced under pressure through the helical coil. The water (permeate) diffuses through the tube wall and is collected at the bottom of the module while the dissolved solids and other impurities leave the end of the coil as a concentrate.



Membrane Module

Fig. 10

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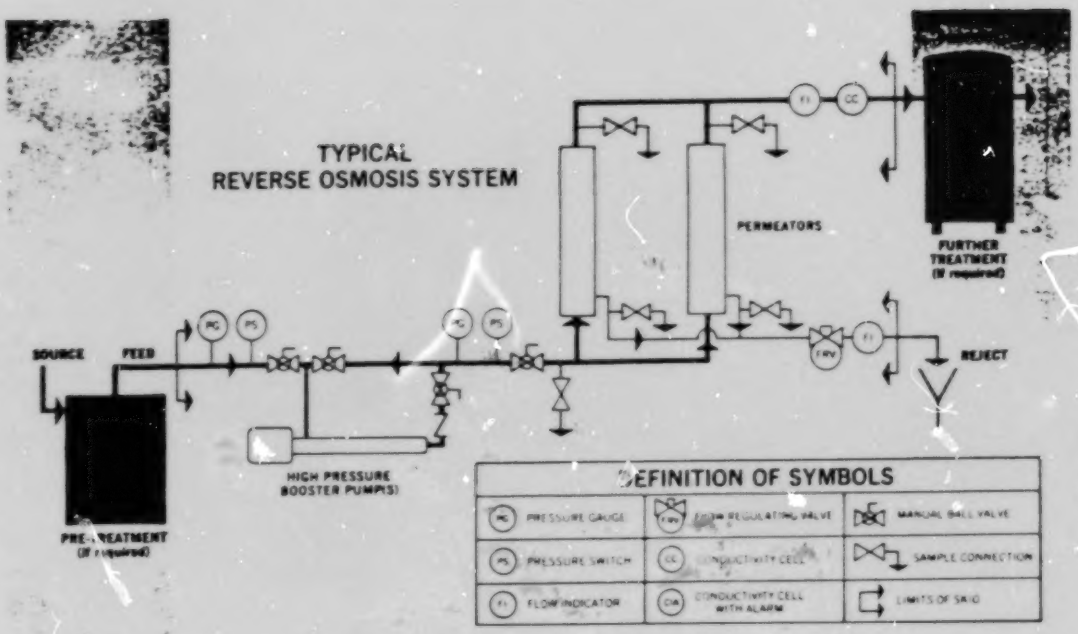

(Permutit Sybron Corporation)

Fig. 11

Fig. 11 is a schematic diagram of a typical reverse osmosis system. The raw water entering may be pretreated by filtration, flocculation, etc., and then is pumped through the membrane modules or permeators. Pressures from 4000 to 10 000 kPa are usually required to push the water through the membrane. The water leaving the permeators will be largely free of dissolved solids and other impurities. Any small amounts of these impurities remaining in the water can be removed by further treatment in an ion exchange demineralizer.

(PE1-2-12-21)

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8. Evaporation

Boilers or steam generators which operate at high pressures and temperatures require make-up water that is free from any impurities. This pure water may be obtained through the use of demineralizers to remove the dissolved solids and deaerators to remove the dissolved gases. Another method which is commonly employed in central stations is to use evaporators instead of demineralizers to obtain water free from dissolved solids and then to use deaerators to remove the dissolved gases.

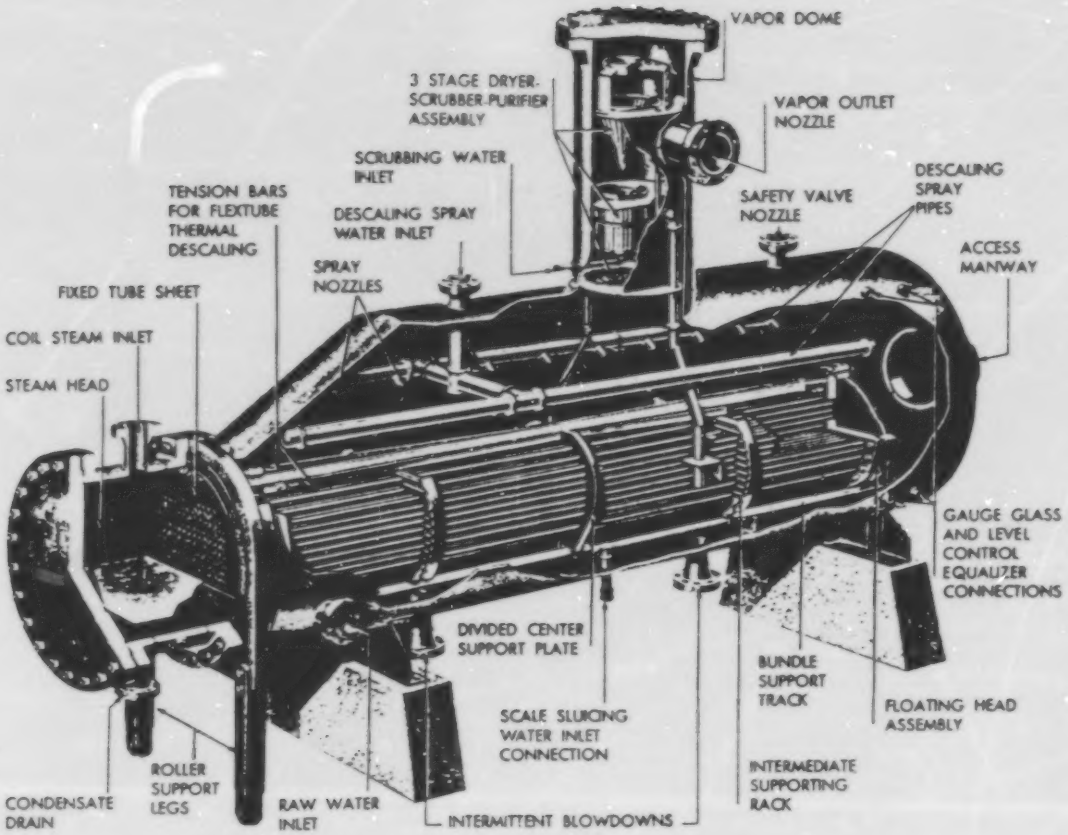
In some cases both methods may be used with a demineralizer being used to "polish" the distilled water obtained by evaporation.

The process which takes place in the evaporator is simply the boiling of the water. The steam or vapor produced from this boiling will be free from solids and when subsequently condensed will form solids-free (distilled) water. Any dissolved gases present in the water, however, will pass off with the vapor produced in the evaporator and consequently the distilled water must be deaerated before going to the boiler. The impurities left behind in the evaporator will form scale and therefore the water fed to the evaporator is usually softened in order to reduce the amount of scale formed.

In spite of water softening treatment prior to evaporation, scaling of the waterside heating surfaces occurs in many cases. This may be caused by small quantities of calcium and magnesium salts which pass through the softening plant. This scale may be cracked off the tubes in some instances by shutting down the evaporator and quickly filling it with cold water. However, if the scale is a hard tenacious type such as a silicate, it will probably be necessary to resort to acid cleaning to remove it.

The various parts of an evaporator are shown in Fig. 12.

In a central generating station the evaporator is installed as part of the regenerative cycle. The coil steam for the evaporator is bled from some stage of the turbine and the vapor produced by the evaporator is condensed in a low pressure feedwater heater.



Evaporator

Fig. 12

9. Mechanical Deaeration

The principle cause of corrosion in boilers is dissolved oxygen in the water. Another cause is dissolved carbon dioxide in the water although it is estimated that carbon dioxide is only one fifth to one tenth as corrosive as dissolved oxygen. If both these gases are present in the water simultaneously then they are much more corrosive than if they existed separately. Another undesirable gas is ammonia which will pass over with the steam from the boiler and attack copper and copper alloys such as contained in valves and condenser tubes.

(PE1-2-12-23)

The term mechanical deaeration refers to the removal from the water of dissolved gases, such as oxygen, carbon dioxide and ammonia, by raising the temperature of the water to the boiling point and allowing the gases thus released to be vented to the atmosphere. The process is assisted by scrubbing the water with a flow of steam in order to sweep away the released gases from the water.

Deaeration principles show that gas removal from water depends upon three factors: whether the gas ionizes in the water or is dissolved as a free gas; the relative pressures of the gas in the water and in the atmosphere; and the water temperature.

Oxygen does not ionize in the water, but exists as a free dissolved gas. Carbon dioxide and ammonia, however do ionize in the water, with only a portion of their total content remaining in the free form.

Only the gases in the free form can exert pressure in the water, so only that portion of the gases present in the free form can be removed by mechanical deaeration. Therefore, oxygen can be reduced to very low concentrations in a deaerator, while carbon dioxide and ammonia can be removed only to the extent that they are present in the free form.

The temperature of the water greatly affects the solubility of gases as at the saturation temperature all free gases are theoretically insoluble. Thus raising the water to the boiling point at any specific pressure will drive off the gases.

The construction of a deaerator usually involves four sections; a section where the water is heated to the boiling point, a section where the released gases are scrubbed from the water, a section for the storage of the deaerated water and a section for condensing any steam that is being carried to the vent with the released gases.

Deaerators are classed as spray type or tray type.

In the spray type the entering water passes through spray valves and is therefore in a finely divided state. It is then heated by coming in contact with steam in the heating section. The water then passes to the scrubber section where it is scrubbed by the entering steam and the gases released by the heating are removed. The deaerated water then passes to the storage section and the steam flows from the scrubbing section to the heating section where it heats the

incoming water spray and where most of it condenses. The gases released in the scrubbing section flow to the vent condensing section where any steam present is condensed and the gases are cooled to some extent. The gases then pass out through the vent.

In the tray type deaerator the process is much the same except that the water, instead of passing through spray nozzles, is broken up by trickling down over a series of trays. The entering steam scrubs the water in the lower tray section and heats the water in the upper tray section. The released gases and some steam pass to the vent condensing section where the steam is condensed and the gases pass to the atmosphere through the vent opening.

Condenser deaeration is another method which is sometimes used in large thermal generating plants. Surface condensers equipped with deaerating hot wells for feedwater may be used to eliminate the separate deaerator. With this design the condensate falls into the hot well through a steam atmosphere. The gases released are then removed by an air ejector.

Internal Methods

Internal treatment of boiler feedwater refers to the method whereby the water is softened, deaerated and conditioned after it has entered the boiler. This is accomplished by adding suitable chemicals to the water in the boiler. In some cases, as with low pressure boilers, this internal treatment is often the only method used to prevent scale, corrosion and sludge formation. Usually however, both internal and external methods are used for medium and high pressure boilers. For example, a high pressure boiler might require water that has been filtered, softened, distilled and deaerated by external methods and in addition require internal chemical treatment to take care of any small amount of impurities left in the water after the external treatment.

In the following paragraphs, the use of internal treatment for pH control, scale prevention, sludge conditioning, deaeration, prevention of foaming, prevention of caustic embrittlement and prevention of return line corrosion is discussed.

1. pH Control

The tendency for boiler water to attack boiler metal increases as the pH value of the water decreases. This corrosion can be prevented by increasing the boiler water pH by the addition of an alkali and it has been found that a pH value of about 10.5 is high enough to do this.

The use of sodium hydroxide to provide the necessary pH value has the longest history of application. In present day practice however, it is the least preferred method of establishing correct pH values because of concern about caustic embrittlement.

Caustic embrittlement is a form of intercrystalline cracking which occurs below the water level and in joints or seams into which boiler water may leak and become concentrated. It is generally thought that the following four conditions are necessary simultaneously to develop caustic embrittlement.

(a) The boiler water must contain substances, particularly hydroxides, capable of producing intergranular damage when concentrated in contact with stressed steel.

(b) There must be a joint or seam into or through which leakage of this boiler water may occur.

(c) The boiler water must concentrate within the joint or seam.

(d) The steel must be overstressed locally where it is exposed to concentration of chemicals.

To avoid the negative effects of sodium hydroxide in regard to caustic embrittlement, the boiler water pH can be adjusted by the addition of sodium phosphates. These phosphates are normally used in any event for the control of scale deposits in the boiler and by their use for this purpose the boiler pH is usually automatically established.

2. Scale Prevention

Boiler scale is caused primarily by the salts of calcium and magnesium. Secondary causes of scale are silica and oil but these latter two are best handled by removing them from the boiler feedwater by external methods.

The calcium and magnesium salts are prevented from forming scale on the boiler surfaces by precipitating them as a sludge and removing this sludge by the boiler blow-off.

The most common chemicals used for this precipitation are the sodium phosphates which include trisodium phosphate, disodium phosphate, sodium metaphosphate and monosodium phosphate. On entry into the boiler all these phosphates are converted to trisodium phosphate which reacts with the calcium and magnesium as follows:

1. Calcium sulphate + Trisodium phosphate ⟶ Tricalcium phosphate + Sodium sulphate

$3\ Ca\ SO_4 + 2\ Na_3\ PO_4 \longrightarrow Ca_3\ (PO_4)_2 + 3\ Na_2\ SO_4$

2. Magnesium Carbonate + Trisodium phosphate ⟶ Trimagnesium phosphate + Sodium carbonate

$3\ Mg\ CO_3 + 2\ Na_3\ PO_4 \longrightarrow Mg_3\ (PO_4)_2 + 3\ Na_2\ CO_3$

Sodium hydroxide will also react with magnesium to form the precipitate magnesium hydroxide as follows:

3. Magnesium carbonate + Sodium hydroxide ⟶ Magnesium hydroxide + Sodium carbonate

$Mg\ CO_3 + 2\ Na\ OH \longrightarrow Mg\ (OH)_2 + Na_2\ CO_3$

The magnesium hydroxide is preferred as a precipitate over the magnesium phosphate which has a very sticky constituency.

Also if sodium hydroxide is present, instead of tricalcium phosphate the precipitate formed in reaction (1) above will be a mixed phosphate and hydroxide precipitate which is preferred because it is less sticky than tricalcium phosphate.

The sludge that is produced by the precipitating of the scale forming compounds in the boiler must be conditioned so that it will stay fluid and well dispersed. In this way the sludge will be easily removed from the boiler through the blow-off connections. The chemicals used for this purpose are usually organic compounds such as starch, tannin, lignin and alginates. Starch is produced from corn, potatoes, etc., lignin and tannin from wood, the alginates from seaweed. These organic materials coat the scale precipitates preventing them from adhering to the boiler plates and tubes.

Another method of scale prevention is by the use of chelating agents. These are chemicals which have the ability to react chemically with the scale forming metal ions of calcium and magnesium and hold them in solution in the boiler water thus preventing them from depositing on the boiler surfaces. Since precipitation of the scale-forming ions does not occur, the total dissolved solids content of the boiler water increases. Because of this, an antifoam agent should be used in conjunction with the chelating agents in order to reduce the possibility of carryover.

There are a great many chelating agents available but two which are commonly used are ethylene-diamine tetraacetic acid (EDTA) and nitrilo triacetic acid (NTA) which are both complex organic chemicals.

These chelating agents are relatively costly and some form of external softening is normally used in order to reduce the amount of chelant required in the boiler.

Chelants can also be used for removal of existing sludge and scale deposits from a boiler without removing the boiler from service. The quantity of deposit to be removed must be considered and a sufficient amount of chelant fed to the system to provide not only complete chelation of the metal ions in the feedwater but also to provide additional chelant to react with the deposit. Caution must be exercised during the cleanup program to avoid removal of old deposits in chunks which could accumulate and restrict circulation. Care must be taken also to prevent high concentrations of chelant which could lead to attack of boiler metal.

As chelating agents are relatively expensive, a careful survey should be made of the feedwater to determine its total hardness. If the hardness of the feedwater is consistently greater than 2 ppm the cost of a chelating treatment program may be excessive. If iron oxides are a significant part of the boiler deposit, the chelating agents will not be effective as they do not chelate ferric iron. However, they are effective in removing calcium and magnesium at the pH values and alkalinity normal to boiler operation.

In comparison to conventional treatment methods, chelants require closer control, demand specific feeding conditions and present potential corrosion hazards. Their use must be supplemented with antifoam materials, oxygen scavengers and a complete condensate corrosion control program.

Complete oxygen removal is especially important as oxygen seriously hampers the effectiveness of chelation.

In regard to the use of chelating agents for cleaning boilers in operation the requirements are: an adequate amount or concentration of the agent, positive contact with the deposit to be removed and sufficient time. Caution must be exercised as mentioned previously as an attempt to clean too rapidly can free large particles of deposit which may block tubes and result in failure. Before proceeding with on-the-line cleaning samples of the boiler deposit should be obtained and analyzed in order to ascertain the time required and the concentration of the agent desired.

(PE1-2-12-28)

Chelating agents require special feeding conditions as they are quite corrosive to carbon steel in the concentrations normally required. A stainless steel quill or nipple should be used at the point where the chelant is injected into the feedwater. The positive displacement chelant pump should also be of stainless steel as well as the tubing from the pump to the injection quill. The chelant solution tank should be plastic or plastic lined.

3. Oxygen Scavenging

Dissolved oxygen enters the boiler system with the makeup water and also by means of air infiltration of the condensate system. This dissolved oxygen will cause corrosion in the feedwater line, closed heaters, and in the economizer. In the boiler a portion of the oxygen will flash and leave with the steam. The remaining portion will attack the boiler metal usually adjacent to the water level in the drum. One of the most serious aspects of oxygen corrosion is that it usually occurs as pitting with the attack concentrated in a small area of the metal surface resulting in comparatively deep holes.

The first and most important step in eliminating dissolved oxygen is mechanical deaeration of the boiler feedwater. However, it is advisable to follow this mechanical deaeration by chemical deaeration or scavenging to remove the last traces of dissolved oxygen.

Sodium sulphite is the chemical agent most commonly employed for chemical deaeration due to its low cost, ease of handling and its lack of scale forming properties. The oxygen scavenging characteristic of sodium sulphite is illustrated by the following reaction:

Sodium sulphite + Oxygen ⟶ Sodium Sulphate

$$2\,Na_2SO_3 + O_2 \longrightarrow 2\,Na_2SO_4$$

To assure complete oxygen removal, it is necessary to maintain a residual concentration of sulphite in the boiler water. The residual required depends on a number of factors such as the method of feed and the point of application, the dissolved oxygen concentration and the variation in the dissolved oxygen concentration of the feedwater.

(PE1-2-12-29)

Continuous feed of sodium sulphite is generally required for complete oxygen removal. In the majority of plants, the most suitable point of application is the storage compartment of the deaerating or open heater. In other plants, sufficient reaction time will be allowed with application to the suction side of the boiler feed pump. While intermittent application is generally not recommended, it has been found in some low pressure systems that adequate protection is provided as long as the additions of sodium sulphite are made with sufficient frequency to continuously maintain the proper residual concentration in the boiler water.

When feedwater is employed in desuperheating, it is desirable to feed sodium sulphite after the point from which the feedwater for desuperheating is taken so as to avoid adding solids to the water.

The sodium sulphate produced in the reaction of sodium sulphite with oxygen adds to the dissolved solids in the boiler water and this is a disadvantage. Also, in very high pressure boilers, the sodium sulphate will form sulphur dioxide SO_2 and hydrogen sulphide H_2S which pass over with the steam and produce return line corrosion.

In the case of high pressure boilers, hydrazine is often preferred to sodium sulphite for removing dissolved oxygen. Its reaction with the dissolved oxygen is as follows:

Hydrazine	+	Oxygen	⟶	Water	+	Nitrogen
N_2H_4	+	O_2	⟶	$2\,H_2O$	+	N_2

Hydrazine is a strong alkali and must be handled with care. As it is extremely flammable in its pure state it is supplied as a dilute solution. When removing the solution from its container, the handler should wear protective clothing including rubber gloves and goggles.

4. Carryover Prevention

The terms carryover, foaming and priming are closely associated and each term is used in describing conditions which result in the entrainment of boiler water solids with the steam.

Foaming is the condition resulting from the formation of bubbles on the surface of the boiler water causing entrainment of boiler water with steam.

Priming is a more violent and spasmodic action causing slugs of water to pass over with the steam.

Carryover is the term applied to the steady entrainment of a small quantity of boiler water solids with the steam. However, it is commonly used to describe the general conditions of contaminants carried over with the steam.

When boiler water solids are carried over in the steam, deposits will occur in non-return and stop valves, superheaters, steam piping and engines or turbines. Such deposits can promote failure of the superheater tubes and loss in engine or turbine efficiency.

Foaming or priming of the boiler water can result in a false water level reading while the thermal shock resulting from slugs of water entering the steam distribution system as a result of priming can seriously endanger all steam driven equipment.

Carryover may result from mechanical and chemical causes or from a combination of the two. Among the mechanical causes of carryover are boiler design, high water level, method of firing and load characteristics. Among the chemical causes are high total solids of the boiler water, high suspended solids, high alkalinities, oil and improper type of external or internal chemical treatment.

Of these chemical causes it is generally agreed that suspended solids contribute most to producing carryover.

Oil present in boiler water is highly undesirable from the standpoint of carryover. Saponification of compounding agents by the alkalinity of the boiler water will produce a soap, thereby causing a foaming effect.

Internal boiler water treatment with phosphate control is standard for most types of feedwater. However, there is a tendency for the precipitated, finely divided calcium phosphate to stabilize boiler water foam, thus contributing to carryover of boiler water solids with the steam. This carryover tendency must be controlled by increased blow-down to lower suspended solids concentrations or by the use of organic agents to control this increased foam load.

Alkalinity as a contributing factor to carryover can also be corrected by adjustment or changes in internal and/or external treatment facilities. If the alkalinity is a result of the internal treatment program the use of less alkaline materials will correct the condition. Should the cause be external, additional facilities may be required such as the installation of a hydrogen zeolite unit to operate in parallel with a sodium unit thereby reducing the total alkalinity of the treated water.

(PE1-2-12-31)

The prevention of carryover difficulties due to the presence of oil in the boiler water is a problem that must be handled entirely external to the boiler itself. No method of internal treatment can be relied upon to overcome a carryover problem caused by oil contamination and the only safe policy that can be followed is the removal of the oil from the boiler feedwater.

Anti-foam Agents

Frequently the cause of a carryover problem cannot be economically corrected through adjustment in boiler water balances or installation of additional external treatment facilities. In many such instances the use of effective anti-foam agents has provided the desired result.

During recent years highly effective organic anti-foam agents have been developed. In general the polymerized esters, alcohols and amides are the most effective agents yet developed.

These agents have the effect that fewer but larger steam bubbles are generated and these bubbles readily collapse in place on the heating surface without leaving that surface and rising through the boiler water.

In addition to the benefit of high purity steam, the use of anti-foam agents frequently results in economic benefits due to reduced blow-down requirements, as boiler water concentrations can be carried at much higher levels without compromising steam purity.

5. Return Line Corrosion

The principal causes of return line corrosion are carbon dioxide and oxygen in solution in the condensate.

In general, the elimination of oxygen from condensate systems can be readily achieved by mechanical or chemical deaeration.

The chief source of carbon dioxide is the bicarbonate and carbonate alkalinity of the makeup water to the boilers. The bicarbonate and carbonate alkalinity when subjected to boiler temperature undergo thermal decomposition and liberate carbon dioxide which becomes entrained with the steam. The other possible and usually minor sources of carbon dioxide are the free, gaseous carbon dioxide that is dissolved in most natural waters and the carbon dioxide which forms from decomposition of soda ash that may be used for regulation of boiler water alkalinity.

Chemicals that can be used for combatting CO_2 corrosion include ammonia, neutralizing amines, and filming amines.

Ammonia can be fed to the system as ammonium hydroxide or ammonium sulphate. At boiler temperatures the ammonia is liberated and passes off with the steam from the boiler and thus is able to neutralize the CO_2. The use of ammonia for this purpose is however, limited due to the fact that it is very corrosive to copper and zinc bearing metals.

Neutralization of CO_2 can safely be accomplished by certain volatile amines such as cyclohexylamine, $C_6H_{11}NH_2$ and morpholine C_4H_9NO. These amines when fed to a boiler volatilize with the steam and combine with the carbon dioxide in the condensate to neutralize its acidity. Unlike ammonia the amines in low concentrations are not corrosive to copper and zinc bearing metals. Control of treatment is usually based on feeding sufficient amine to raise the pH of the condensate to 7.0. Satisfactory reduction of carbon dioxide corrosion is obtained with the use of the neutralizing amines in the absence of oxygen.

The filming amines function on a completely different principle from the neutralizing amines. The filming amines do not neutralize carbon dioxide. Instead, they function by forming on the metal surfaces contacted an impervious non-wettable film that acts as a barrier between the metal and the condensate, protecting against both oxygen and carbon dioxide attack.

The filming amines of value in the prevention of corrosion are the high molecular weight amines and amine salts having straight carbon chains containing 10 - 18 carbon atoms. Octadecylamine $C_{18}H_{37}NH_2$, hexadecylamine $C_{16}H_{33}NH_2$, and dioctadecylamine $C_{36}H_{74}NH$, are examples of useful materials of this type. In plant practice the most successful results have been obtained with the dispersed octadecylamine. Condensate should be used in preparing the chemical solution which is then fed with a small chemical pump to the main steam line at a point where it will be well mixed with the steam. The material is dispersed readily with the steam and is carried through the steam and condensate lines, forming a non-wettable film on the metal surfaces contacted.

BOILER WATER AND STEAM SAMPLING

In order to determine the conditon of the boiler water and the purity of the steam from the boiler, proper representative samples of each must be obtained and then submitted to the appropriate test.

Water Sampling

To obtain a representative sample of the water in the boiler drum an internal pipe should be used extending along the length of the drum. The pipe should have one end sealed and should have a number of inlet holes along its length, having a total area of about 50 per cent of the pipe area. Alternatively the sample may be obtained from the continuous blow-down pipe. Any sampling pipes located external to the boiler drum must be able to withstand maximum boiler pressure.

Samples obtained should be cooled to room temperature in a cooler coil which is equipped with a throttling valve at its outlet. In this way the sample remains under full pressure until it has cooled to a point where it will not flash. The cooler inlet should be equipped with a shutoff valve.

Sample coolers are usually made of two continuous lengths of copper or stainless steel tubing, one inside the other. The sample should be brought in at the top and leave at the bottom and the cooling water should flow counter to the sample flow. The cooling water supply should be dependable and adequate enough to cool the sample to 21°C.

Steam Sampling

Impurities in steam are usually in the form of water droplets or small dry particles. If it is desired to take samples from a pipeline, they should be withdrawn from a long vertical run where the particles and droplets are mixed across the pipe area in preference to a horizontal run where the particles and droplets tend to concentrate along the bottom of the pipe. Samples may also be taken from the steam drum by means of sampling lines installed after the steam separating equipment. Stainless steel pipe should be used for high temperature steam sampling. Steam samples are condensed and cooled in coolers and the cooling coil should be arranged so that the condensate can pass continuously through a conductivity cell. There should also be a parallel connection for delivering the condensed and cooled sample to a sampling flask or to waste.

The cooling coil must be supplied with an adequate and dependable source of cooling water as failure of supply could result in overheating and damage to coil and conductivity cell.

Sample Testing Precautions

In order to obtain accurate results the sample testing procedure must be carefully carried out. Testing errors may be caused by poor sampling methods, contamination of samples, use of weak or improper reagents, and failure to follow testing instructions.

Sample containers and connecting tubing must be thoroughly cleaned and rinsed out several times with the water or condensate being collected. The samples should not be exposed unduly to the air and should be cooled to 20°C or below during collection otherwise a vacuum will develop in the flask as it cools which may draw in contaminating air.

Also to avoid contamination, the sample tubing and flasks should be completely free of air bubbles.

The samples should be tested in a cool, clean, well ventilated space which is equipped with a sink, storage facilities, electrical outlets, proper working surfaces, hot and cold running water, and a supply of distilled water.

QUESTION SHEET

POWER ENGINEERING

First Class
Sect. 2, Lect. 12

1. Discuss the three classes of water impurities and the general method used to treat each type.

2. Sketch and describe a method for removing suspended impurities from water.

3. (a) Describe the essential equipment and operation of a hot lime-soda softener.

   (b) List the equations for the chemical reactions involved in hot lime-soda softening.

4. (a) Explain the difference between the hot lime-soda and the hot lime-hot phosphate processes.

   (b) List the equations for the chemical reactions involved in the hot lime-hot phosphate process.

5. Describe the principle of ion exchange and describe some type of ion exchange softener including the equations for the chemical reactions involved.

6. Explain the meaning of the term demineralization and describe briefly how it can be accomplished.

7. Sketch and describe a typical reverse osmosis system.

8. Discuss the principles of deaeration and describe briefly two methods by which it may be accomplished.

9. Explain what is meant by internal water treatment and explain the functions of this type of treatment.

10. Describe the equipment involved and the operation of the water treatment system in the plant in which you are employed.

(PE1-2-12-Q)

12.3

FEEDWATER — TESTING

Goal:

The student will be able to describe tests on feedwater.

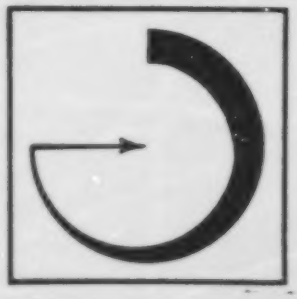
Performance Indicators:

1. Identify common test equipment, reagents and indicators.
2. Describe standard tests of water quality.

Study Guide

* Read the goal and performance indicators to find what is to be learned from package.
* Read the vocabulary list to find new words that will be used in package.
* Read the introduction and information sheets.
* Complete the job sheet.
* Complete self-assessment.
* Complete post-assessment.

Vocabulary



* Acidic
* Alkalinity
* Ammonium molybdate
* Burette
* Caustic alkalinity
* Excess phosphate
* Excess sodium sulphite
* Hydrogen ion concentration
* Indicator
* mho
* Phenolphthalein alkalinity
* pH value
* Pipette
* Sequestering agent
* Soap test
* Titration
* Total alkalinity
* Total content of dissolved solids
* Total hardness

Introduction

Feedwater testing requires exacting procedures. Testing is a laboratory function that requires clean equipment, careful sampling procedures and exact measurements.

This package is designed to introduce the apprentice to the purpose and types of tests used in maintaining the purity of boiler feedwater. Testing procedures should be obtained from test kits, manufacturers or the reference material., These specific testing instructions should be followed closely until experience has been acquired.

Information

Test Equipment Needed

- Sampling bottles
- Test tubes
- Porcelain dishes
- Pipettes
- Burettes
- Reagents
- Indicators
- Elecronic instruments

Reagents

A reagent is used to produce a chemical reaction in water. Some standard reagents used in water tests are:

- Sulphuric acid N/50
  Silver nitrate
  Potassium — iodide-iodate solution
  Ammonium molybidate solution
  Soap solution

Indicators

Indicators are solutions that cause changes in color in a water sample depending on the Ph of the samples. Most test kits will include the following indicators.

- Phenolphthalein
- Methylorange solution
- Starch solution
- pH indicator solutions

Types of Tests

The following tests are normally carried out in testing the quality of boiler water.

- Total content of dissolved solids
- Total hardness
- Alkalinity
- Chlorides
- Excess sodium sulphite

Information

- Excess phosphate
- pH value

Total Content of Dissolved Solids

The total content of dissolved solids is usually measured by the electrical conductivity of the liquids. Solids in water offer greater electrical conductivity to a current and is measured in mho's. This term is Ohm's spelled backwards since conductivity is the opposite of resistance. Clear water is more resistant to the passage of electricity than water with solids. Instruments are available for measuring conductivity.

Total Hardness Test

The total hardness test is a measure of the salts of calcium and magnesium that are present in the water. A "soap test" uses a standard soap solution which is mixed with the water sample. The amount of soap solution needed to neutralize the hardness of the water determines the hardness of the water. The total calcium and magnesium content can also be measured by titration. A sequestering agent is mixed with the water sample in measured amounts. An organic dye will cause a change in water color from red to blue. The amount of sequestering agent used determines the hardness of the water. A formula is used for calculating the hardness of the water.

Alkalinity

Alkalinity measurements require three types of tests. The operator must determine the levels of bicarbonates, carbonates and hydroxides that are present in the water. Water treatments will differ according to the presence of these products. The tests are:

- Phenolphthalein alkalinity test for hydroxides and carbonates
- Total alkalinity for total quantity of all dissolved salts
- Caustic alkalinity for total hydroxide quantity

Chloride

This test is used to determine the rate of blow-down for a boiler. Chlorides do not precipitate which makes them a reliable indicator for calculating blow-down.

$$\frac{\text{Chlorine in feedwater}}{\text{Chlorine in boiler water}} \times 100 = \% \text{ blow down}$$

Information

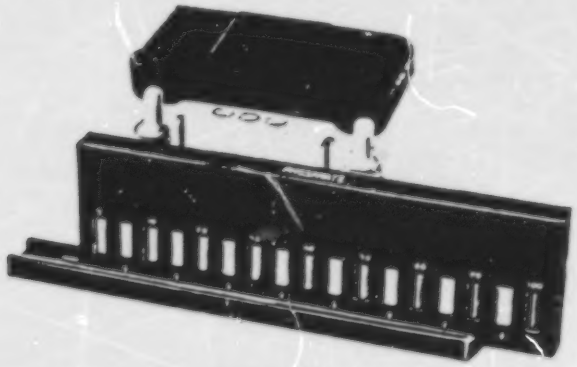
The sample is made slightly acidic by the addition of mild sulphuric acid. It is then titrated with silver nitrate until the color changes. The chlorine content can then be calculated.

Excess Sodium Sulphite

Oxygen causes corrosion inside the boiler. In order to hold down the oxygen levels, the feedwater must be tested for oxygen content. Sodium sulphite can be used to dissolve the oxygen in the water and convert it to a sulphate form. However, excess sodium sulphite can be acid forming and harmful. It is desirable to keep the sodium sulphite levels at very slightly excess levels so that oxygen will be controlled and acid conditions will be avoided. The test for excess sodium sulphite involves titrations with potassium iodide-iodate solution on samples that have been mixed with a starch solution.

Phosphate Solution

Sodium phosphates are used in boilers to precipitate calcium salts into calcium phosphates to prevent the formation of scale. It is desirable to have an excess of sodium phosphate in the boiler water at all times. Potassium nitrate crystals are mixed with the water sample and then combined with an ammonium molybdate reagent. The sample is observed for a condition of cloudiness. The time required for the cloudiness condition to occur shows whether the boilerwater has an adequate reserve of sodium phosphate. Another test can be conducted by making color comparisons on a Taylor phosphate comparator. The comparator uses standardized colors to measure the sample.

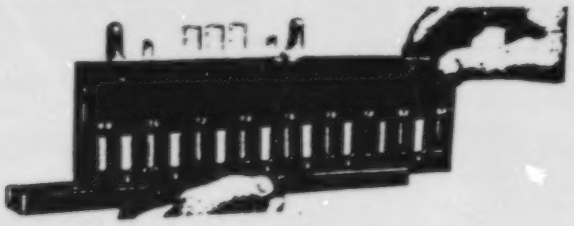


Taylor Phosphate Comparator

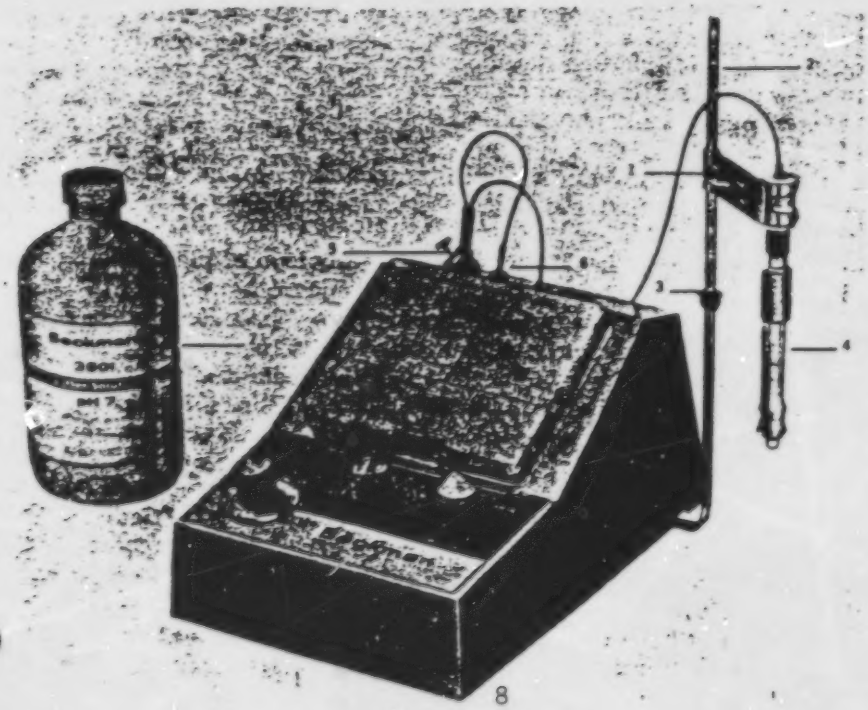
Information

pH Value

Acid conditions inside a boiler enhance corrosion. Whether the feedwater is acidic or alkaline is measured by a term pH. pH actually means hydrogen ion concentration. A pH value of 7.0 is neutral. Anything below 7.0 is acidic and everything greater than 7.0 is alkaline. pH can be measured by either colorimetric or electronic methods. Colorimetric tests involve adding indicator solutions to samples in test tubes.



Electronic tests are conducted by a pH meter such as the one shown below.



1. Electrode Clip
2. Support Rod
3. Electrode Stop
4. Combination Electrode
5. Glass Electrode Terminal
6. Reference Electrode Terminal
7. Buffer Solution

8

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Assignment

* Read pages 3 - 19 in reference.
* Complete the job sheet.
* Complete self-assessment and check answers.
* Complete post-assessment and have instructor check answers.

Job Sheet

CONDUCT pH VALUE TESTS

* Conduct colorimetric test

  - Set up test tube rack (from test kit)
  - Fill 6 test tubes with 10ml of boiler water samples
  - Fill 1 test tube with 10ml distilled water
  - Add .5 ml of indicator to a test tube
    Repeat with each type of indicator with only one indicator per test tube
  - Select the test tube which shows a color change
  - Place that test tube in a comparator and find color range

* Conduct pH meter test

  - Read instructions with pH meter to be used
  - Conduct test three times and calculate mean or average
  - Compare pH value of pH meter test with colorimetric test

Self Assessment

Match the following terms with descriptive phrases.

____ 1.	mho	A. A reagent used in chloride tests.
____ 2.	Reagent	B. A reagent used in testing for excess sodium sulphate.
____ 3.	Indicator	C. A reagent used in testing to test for phosphates.
____ 4.	Silver nitrate	D. Produces a chemical reaction in water.
____ 5.	Potassium-iodide-iodate	E. Total hardness test to measure calcium and magnesium salts in water.
____ 6.	pH	F. Unit of measurement for electrical conductivity.
____ 7.	Phenolphthalein alkalinity tests	G. Causes changes in color of water.
____ 8.	Ammonium molybdate	H. Measurement of hydrogen ion concentration.
____ 9.	Caustic alkalinity tests	I. Tests for hydroxides and carbonates in water.
____ 10.	Soap test	J. Tests for total quantity of hydroxides in water.

Self Assessment Answers

F 1.

D 2.

G 3.

A 4.

B 5.

H 6.

I 7.

C 8.

J 9.

E 10.

Post Assessment

1. Silver nitrate and ammonium molybdate solution are _____.

2. Phenolphthalein and methylorange solutions are _____.

3. The unit of measurement for electrical conductivity (total dissolved solids) is _____.

4. The mixing of a liquid into another liquid in measured amounts until a color occurs is called _____.

5. Three types of alkalinity tests are needed to measure levels of carbonates, bicarbonates and _____.

6. The rate of blow-down for a boiler can be determined by a _____ test.

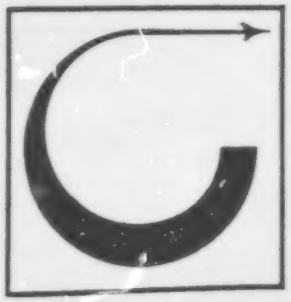
7. Sodium sulfite tests requires titrations with _____ _____ _____ solutions.

8. Sodium _____ are commonly used in boilers to precipitate calcium and prevent scale formatons.

9. The pH value of water can be determined by _____ or _____ methods.

10. Hydrogen ion concentrations of liquids are commonly expressed as _____ values.

Instructor Post Assessment Answers



1. Reagents
2. Indicators
3. mho
4. Titration
5. Hydroxides
6. Chloride
7. Potassium iodide-iodate
8. Phosphate
9. Colorimetric or electronic
10. pH

Supplementary References

* Corespondence Course. Lecture 7, Section 2, Second Class. Steam Generators. Southern Alberta Institute of Technology. Calgary, Alberta, Canada.

SOUTHERN ALBERTA INSTITUTE OF TECHNOLOGY
CALGARY ALBERTA

Correspondence Courses
Power Engineering

SECTION 2

STEAM GENERATORS

Second Class
Lecture 7

BOILER FEEDWATER TREATMENT

Feedwater

Water is a substance which must be considered as a dilute solution of chemicals until it has been treated in some way to render it pure. Further, most of the chemicals in solution have undesirable properties when their concentration is increased by evaporation in the boiler plant.

The natural sources of water may be subdivided into the following categories:

1. Rain water
2. Hard water
3. Soft water, and
4. Estuarine water.

From a chemical viewpoint rain water contains the least constituents, but raw rain water is corrosive by virtue of its carbon dioxide and oxygen contents and in industrial atmospheres some sulphur acids may also be present.

Hard water is derived from rain water which has percolated through the earth and has leached out some sulphates, chlorides, and carbonates of calcium and magnesium. The bicarbonates impart what is known as temporary hardness, the sulphates and chlorides make permanent hardness.

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Soft water is rain water which has percolated over insoluble rocks. This water while free of calcium and magnesium salts may carry other compounds, for example organic material derived from decomposition of vegetation, some salts such as sodium chloride and sodium sulphate together with ammonia and silica. The corrosive carbon dioxide originally in the rain water is still present and the pH or acidity of the water will depend to a large extent on the nature of the earth and rock through which it has percolated.

Estuarine water is in fact diluted sea water, the amount of dilution depending upon the plant location (distance from the sea coast) and varying with the ocean tides. The chemical concentrations of such waters are generally greater than the others already considered and great care has to be taken to render them suitable for feedwater. Due regard must also be paid to the nature of any industrial effluents which may be present.

Thus it can be said that all natural waters require treatment to some degree before being suitable for boiler feedwater, the extent of the treatment depending upon the solutes present.

Aims of Boiler Water Treatment

The principal aims of boiler water treatment may be summarized as follows:

1. The complete removal of all scale-forming salts from the boiler water.

2. The elimination of acid-corrosion tendencies through the maintenance of an adequate reserve of alkalis in the water.

3. The reduction of dissolved oxygen to a minimum.

4. The regulation of the quantity and quality of the total dissolved solid contents of the boiler water.

In order to accomplish these aims the available feedwater must be tested for impurities, a course of treatment prescribed depending upon these findings, and finally a series of tests set up to check that the desired results are being achieved.

Such a program can only be developed by a professional water treatment chemist. Attempts at prescribing water treatment by any but the best informed personnel are likely to be inadequate and may well be extremely costly in terms of plant repair.

The power engineer must however understand the processes which are involved and be able to apply the correct techniques once the required treatment has been prescribed.

This in turn demands a knowledge of the tests which can be applied to measure the effectiveness of the treatment.

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WATER TESTING

It may be easier to obtain a clear picture of boiler water treatment methods by first gaining an understanding of the tests used and the optimum figures aimed at. With this in mind the following paragraphs describe boiler water testing methods commonly used.

Testing Equipment

Test kits comprise sampling bottles, test tubes, porcelain dishes, burettes and pipettes, and other glassware usually found in laboratories and include standard reagents and indicators. In modern installations, in addition to such test kit, sensitive electronic instruments are also provided.

Reagents

A reagent is a substance which, on account of its known chemical properties, is employed to produce specific reactions in combination with particular constituents of water which it is desired to measure. The reaction is observed and the quantity of the reagent required to produce it recorded, so that a calculation can be made as to the quantity of the constituent under measurement. Thus, a reagent serves as a measuring instrument. In consequence, its quality and strength must conform exactly to specifications laid down.

As most reagents are solutions of acids or alkalis, specifications as to their solution-strength are drawn up with an eye to the facility of calculation of the result subsequent to a test. For instance, N/50 sulphuric acid is used as a reagent in alkalinity tests. The prefix N/50 represents the solution strength of the sulphuric acid, i.e., 0·98 grams of pure sulphuric acid is dissolved in one litre of distilled water. This particular strength is chosen because one mL of this reagent precipitates 10 p.p.m. of $CaCO_3$. A change in strength will obviously change the quantity of precipitation. Hence it is that standards are laid down for the quality and strength of various reagents.

Standardization is a skilled operation. It is, therefore, desirable that the boiler engineer obtains his reagents direct from firms specializing in this commodity. Time has an adverse effect on the strength of reagents. Hence excessive quantities should not be stocked, the maximum stock being limited to six months' requirements.

The principal reagents employed in water test kits are the following:

N/50 sulphuric acid,
Silver nitrate solution,
Potassium-iodide-iodate solution,
Ammonium molybdate solution,
Soap solution.

Indicators

An indicator is a solution which exhibits a change in its color when a very small quantity is dissolved in a sample of water whose acidity or alkalinity is within a known and stipulated range. A number of indicators are available, each changing its color over a different acidity (or alkalinity) range. All of them are organic compounds with complex chemical formulae and are themselves weak acids or alkalis. When added to other solutions, they do not undergo any chemical reaction with any of the constituents of the solution beyond being ionized. The color change is the special characteristic resulting from such ionization.

Indicators find their place in test kits as, with their help, appropriate color changes can be produced and observed so as to decide when titration of the sample with the reagents can be stopped. The principal indicators employed in the different tests are:

Phenolphthalein.
Methylorange solution.
Starch solution.
A set of pH indicator solutions as tabulated under "Test for pH Value".

Titration

Titration is a procedure wherein a standard solution from a calibrated container is slowly added to the water sample. When a visual change in the sample is noted (the end point) the amount of the standard solution used will be proportional to the amount of the impurity present in the sample.

Sampling

It is of little use to carry out analyses carefully and accurately if the samples are not representative. If it is desired to study the effect of a certain addition of treatment chemicals in a boiler, it will not do to take a sample from the boiler immediately after the addition of the chemicals and expect a change in results. Time must be allowed for the change to become effective. Where possible, the samples must be drawn through cooling coils, directly in stoppered glass bottles. Where this is not possible, care should be taken to use only such vessels as are resistant to chemical attack by the constituents of the water.

Except where otherwise specified, all samples must be filtered through a good quality filter paper yielding a clear filtrate. For some tests, e.g. pH value test, filtration is not permissible. In such cases, the suspended matter in the sample must be allowed to settle before removing the portion of the sample necessary for the test.

Units

It has been ironically stated that there are as many methods of expressing water analyses as there are chemists making them. For instance, the quantity of calcium present in a given sample can be expressed in several ways, either directly as the mass of pure calcium, or indirectly as the equivalent mass of different calcium compounds in which the same mass of pure calcium may be said to exist.

In water analysis, the analyst is more concerned with the determination of the properties of the water, its hardness, alkalinity, etc., than with its composition in terms of individual elements. It is convenient, therefore, to reduce all measurements of different salts producing one property into one uniform standard.

The conventional method adopted (with a few exceptions) is to express all the constituents which produce a particular property in terms of their calcium carbonate ($CaCO_3$) equivalents, even though the particular property may have nothing to do with this compound. $CaCO_3$ has a molecular mass of 100 and is therefore a very convenient unit.

Thus, one unit of calcium with a molecular mass of 40 is represented by

$\frac{100}{40}$, i.e., 2.5 units of $CaCO_3$ equivalent.

Similarly, magnesium sulphate ($MgSO_4$) has a molecular mass of 120. Therefore, one part of $MgsSO_4$ is represented by

$\frac{100}{120}$, i.e., 0.833 units of $CaCO_3$ equivalent.

In popular practice, the basic numeral units for water analysis are:

(1) Parts per million (p.p.m.) = number of parts of the substance per million parts of water, both in terms of mass.

(2) Grains per Imperial Gallon = number of grains of substance per 1 British Imperial gallon of water (also in terms of mass).

1 Grain per Imperial gallon = 14.25 grams per cubic metre (g/m^3)

Descriptions of Various Tests

The principal tests on boiler water samples carried out in practice are for the measurement of:

1. Total content of dissolved solids.
2. Total hardness.
3. Alkalinity: (i) Phenolphthalein alkalinity
   (ii) Total alkalinity
   (iii) Caustic alkalinity.
4. Chlorides.
5. Excess sodium sulphite
6. Excess phosphate.
7. pH value: (i) Calorimetric method
   (ii) Electronic method.

In what follows, an attempt has been made to describe briefly each of these tests with particular reference to its purpose, procedure and to the method of interpreting the results of the test.

(PE2-2-7-5)

1. ESTIMATION OF TOTAL CONTENT OF DISSOLVED SOLIDS

Purpose. The quantity of total dissolved solids constitutes a very approximate measure of the influx of scale-forming and corrosive mineral salts with the feedwater.

When other tests such as hardness, alkalinity, etc., are made, the measurement of the density of water is not considered as being of vital importance for the proper operation of the boiler. (Total dissolved solids include all salts in solution irrespective of whether they are considered desirable, undesirable or neutral.) The measurement, however, is made mainly as a cross-check and to assist in keeping the total dissolved solid content below the recommended figures.

Test. The total dissolved solids in a boiler water may be discovered by evaporating a sample to dryness and then weighing the residue when dry. This method is obviously not well adapted to practical boiler house operating conditions because of the extreme accuracy required in weighing.

The method more commonly employed is to measure the conductivity of a water sample and then use this to calculate the solids in solution.

Pure water is highly resistant to the passage of an electric current, however any solids in solution will reduce this resistance proportionately, or stated another way, increase its conductivity.

The basic unit of electrical resistance is the ohm. Since electrical conductivity is the reciprocal of resistance the unique term "mho" (ohm spelled backwards) was chosen as the basic unit.

In the conductivity test an electrical instrument is used, operating on the wheatstone bridge principle, to compare the resistance of a sample of water against a standard resistance. Dissolved solids contents of from 0.5 to 10,000 p.p.m. can be measured using these instruments.

The conductivity test measures the total ionic concentration but since the hydroxide ion (alkalinity) has a much higher conductance than the other ions present, for accurate results the sample must be neutralized before the conductivity test is made (gallic acid is commonly used for the purpose).

Conductivity instruments are usually calibrated in micromhos (a micromho is a millionth of a mho). Calibration directly in p.p.m. of dissolved solids would introduce errors since the conversion from micromhos to p.p.m. will vary slightly with different waters.

For average industrial purposes the conversion factor of 1 micromho equivalent to 0·9 p.p.m. dissolved solids is sufficiently accurate.

The American Boiler Manufacturers Association in its standard guarantee of steam purity stipulates the following maximum limits for solids content of boiler water:

Table 1

Operating Pressure (kPa)			Total Solids (ppm)
2070	-	2070	3500
2070	-	3100	3000
3100	-	4140	2500
4140	-	5170	2000
5170	-	6200	1500
6200	-	6895	1250
6895	-	10 340	1000
10 340	-	13 790	750
13 790	-	———	500

2. HARDNESS TEST

Purpose. Hardness in water is the property which exhibits itself by the non-formation of permanent lather, when mixed with a standard soap solution. Truly soft water will form a persistent lather even with the addition of an extremely small quantity of soap solution, provided the water is agitated sufficiently. Water becomes hard due to the presence, in solution, of one or more salts of calcium and/or magnesium, the more important ones being the bicarbonates, carbonates, chlorides, sulphates and nitrates of the two metals.

Hardness of water may be sub-divided into "temporary" and "permanent" hardnesses. Water is said to possess "temporary" hardness when, on heating the water in open vessels, it is rendered soft. The bicarbonates and carbonates of calcium and magnesium impart temporary hardness to the water which contains them. Hardness due to calcium and magnesium sulphates and chlorides cannot be removed by boiling in open vessels and so it is termed "permanent". Under boiler conditions, however, all hardness salts precipitate and form "scale".

In recent years the terms temporary and permanent hardness have given away to "carbonate" and "non-carbonate" hardness respecitvely.

Carbonates and bicarbonates of both metals form soft, porous scales. Calcium sulphate forms a scale which is hard, non-porous and adherent. Magnesium sulphate and the chlorides of calcium and magnesium break up to form acids and also precipitate soft scales. Scale-formation in boilers, particularly on heating surfaces, is undesirable as it reduces heat-transfer efficiency and causes tube failures owing to overheating of metal. The intensity of hardness in a boiler water is thus a measure of the propensity of the water to form scales on heating surfaces.

Test (Soap Method). When mixed with soap solution, a hard water throws out a precipitate or curd which represents a reduction of soluble hardness salts to insoluble compounds. When all hardness salts are precipitated, the water is rendered soft and so forms a persistent lather with a very small further addition of soap.

This property of soap which enables it to neutralize the hardness salts through precipitation is made use of for the determination of the degree of hardness present in samples of boiler water. The result is expressed in parts of $CaCO_3$ equivalent per million parts of water.

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The test consists of titrating, with a standard soap solution, 100 mL of filtered boiler water taken in a glass-stoppered bottle and shaking vigorously after each addition of 0.2 mL of soap solution until a lather is obtained which persists for at least five minutes when the bottle is laid aside at rest.

Calculation. The quantity of soap required to neutralize the hardness salts through precipitation is directly proportional to the quantity of hardness salts present.

> 1 mL of standard soap solution precipitates 10 ppm of $CaCO_3$. Hence, hardness of sample (expressed in ppm of $CaCO_3$ equivalent) = 10 times mL of soap solution added during test. Standard soap solution precipitates all hardness salts, not only the carbonates.

Test (Titration with a Sequestering Agent). This test is based on the determination of the total calcium and magnesium content of a sample by titration with a sequestering agent in the presence of an organic dye.

The indicator or dye will show a red color if the hardness is present in the sample. titration is then carried out with the hardness titrating solution until the end point shows a color change from red to blue.

Calculation. The quantity of titrating solution used is directly proportional to the quantity of hardness salts present, given a standard quantity of sample. Hence if a 100 mL sample is used, then

$$\text{ppm hardness as } CaCO_3 = \frac{\text{mls titrating solution} \times 1000}{100}$$

The following figures give examples of the range of hardness to be expected:

15 - 60	=	soft water
61 - 120	=	medium hard
121 - 180	=	hard
180 +	=	very hard

3. ALKALINITY

The boiler engineer needs to know the condition of the water with reference to all the three alkalinity measurements, for only then can he determine separately the amount of bicarbonates, carbonates and hydroxides present. This determination is essential in order to decide on the nature of the treatment to be employed. For instance, if the water is found to have caustic alkalinity of a value higher than a stipulated amount, there is danger of a phenomenon known as caustic embrittlement, that is, the boiler metal develops hair-line cracks along grain boundaries. Similarly, if the bicarbonate content is found to be excessive, free carbon dioxide is released, promoting corrosion. The treatment of the water differs in either case and is controlled on the basis of the results of these alkali tests.

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Definitions. An alkaline solution, simply stated, is one which contains hydroxides, carbonates and/or bicarbonates.

As previously stated, alkalinity tests are usually carried out in three different parts, viz (i) Phenolphthalein alkalinity,
(ii) Total alkalinity, and
(iii) Caustic alkalinity.

"Phenolphthalein alkalinity" is the term employed to indicate the alkalinity imparted to water by hydroxides and carbonates only, i.e. excluding bicarbonates.

"Total alkalinity" represents the total quantity of all dissolved salts imparting alkaline properties to the water.

"Caustic alkalinity" measures the quantity of hydroxides present in solution.

Purpose. To prevent corrosion inside a boiler, it is essential that the water inside should not be acidic. Even pure distilled water has a tendency to become acidic due to the breaking up of water molecules under conditions existing in a boiler. It is necessary, therefore, to maintain the boiler water slightly alkaline, i.e. there must be present small quantities of hydroxides, carbonates, and/or bicarbonates in solution.

(i) Phenolphthalein Alkalinity Test

Explanation. When a drop of phenolphthalein, which is itself an alkaline liquid, is added to a water which contains hydroxides or carbonates, the water turns pink in color. This coloring is indicative of a higher alkalinity of the solution than that of the phenolphthalein drop. When an acid is added to the solution so that the alkalis are neutralized or weakened to a strength below that of the phenol drop, the pink color disappears. In the presence of an acid, hydroxides are neutralized and form salts. Carbonates, on the other hand, form into bicarbonates first and then, with the addition of more acid, are neutralized. While carbonates are more alkaline than phenolphthalein, bicarbonates are less alkaline, although even the latter comes under the general category of alkalis. Thus, when an acid is added to the water sample till the pink color produced by a few drops of phenolphthalein just disappears, it is understood that at the moment of the color change, all the hydroxides have been neutralized and all the carbonate molecules have been re-formed into half their number of bicarbonate molecules (i.e. each pair of carbonate molecules couple up to form a single bicarbonate molecule). This property of phenolphthalein changing color is utilized to determine the quantity of carbonates and hydroxides in solution in the boiler water.

Test. The test consists of coloring a measured quantity of the sample with phenolphthalein and then titrating with sulphuric acid until the color just disappears. 100 mL of filtered sample is taken in a porcelain dish and 10 drops of phenolphthalein indicator is added. If the sample is distinctly alkaline, the color will change to pink. (If it does not turn pink, the inference is that phenolphthalein alkalinity is negligible and may be taken as zero). This colored sample is now titrated with N/50 sulphuric acid until the pink color just disappears, the sample being kept stirred all the time. The quantity of acid added is note. The tested sample is retained for further testing.

Calculation. One mL of N/50 sulphuric acid neutralizes 0.001 g of $CaCO_3$. Hence if 1 mL of acid is used in the test, it means that 0.001 g of $CaCO_3$ or its alkaline equivalent is present in solution in 100 mL of water.

100 mL of water has a mass of 100 g.

Hence, phenolphthalein alkalinity per mL of acid used
= 0.001/100 parts of $CaCO_3$ per part of water
= 10 parts of $CaCO_3$ per million parts of water.

Therefore, given that the sample quantity is 100 mL, alkalinity to phenolphthalein (expressed in $CaCO_3$ ppm) = 10 times mL of acid used.

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(ii) Total Alkalinity Test

Explanation. Phenolphthalein does not turn pink in the presence of bicarbonates, even though the latter are alkaline substances. Hence, a phenolphthalein alkalinity test does not measure the total quantity of alkaline substances dissolved in the boiler water under test. Unlike phenolphthalein, methyl-orange reacts even in the presence of bicarbonates. When the water is alkaline, a few drops of this liquid imparts a yellow hue to the water. When the alkalinity is completely neutralized by the addition of an acid, the color of the water changes from yellow to red. This color reaction of methyl-orange is used to measure the total alkalinity of the boiler-water sample.

Test. The test itself is a continuation of the phenolphthalein test, the same sample being further colored with methyl-orange and then the residual alkalinity neutralized. Ten drops of methyl-orange are added. If the sample turns red immediately, it means no bicarbonates are present and that the sample has been neutralized by the addition of acid during the phenolphthalein test. The phenol alkalinity is then also the total alkalinity. If the sample turns yellow, it means that the sample is still alkaline. The sample is then titrated with N/50 sulphuric acid until the yellow color changes to red, and the quantity of acid added from the start of the phenolphthalein test till the end of the total alkalinity test recorded.

Calculation. Therefore using a 100 mL sample, total alkalinity in $CaCO_3$ ppm = 10 times mL of acid used.

(iii) Caustic Alkalinity Test

Explanation. When barium chloride is added to an alkaline sample, the carbonates are precipitated leaving only the hydroxide alkalis (also called caustic alkalis) to be present in solution. A phenolphthalein test carried out after eliminating the carbonates in this manner will give the value of caustic alkalinity in $CaCO_3$ ppm.

Test. 10 mL of barium chloride is added to 100 mL of filtered boiler samples, this quantity of barium chloride being considered sufficient to neutralize the carbonates present. Then, 10 drops of phenolphthalein indicator is added. If the sample does not turn pink, it means that it has no hydroxide content and hence no caustic alkalinity. If the sample does turn pink, it should then be titrated with N/50 sulphuric acid until the pink color just disappears, the sample being kept stirred all the time. The quantity of acid added is recorded.

Calculation. Caustic alkalinity in $CaCO_3$ ppm = 10 times the mL of acid added (using a 100 mL sample).

Interpretation of Alkalinity Tests

Although all the different values of alkalinity as measured above are expressed in parts of $CaCO_3$ per million parts of water, it should be clearly understood that $CaCO_3$ is used only as a unit of measurement and that the alkalinity of the water may be due to dissolved hydroxides, carbonates or bicarbonates of calcium, sodium, magnesium, etc.

Bicarbonates and hydroxides cannot co-exist in solution, as the latter convert the former into carbonates through chemical combination as follows:

$$Ca(HCO_3)_2 + Ca(OH)_2 \longrightarrow 2\,CaCO_3 + 2H_2O$$

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If C, P and M are respectively the values of caustic alkalinity, phenolphthalein alkalinity and total alkalinity (all in $CaCO_3$ ppm) the results are interpreted as follows:

(i) If C = nil, carbonate content = 2P; bicarbonate content = M - 2P. P is less than 1/2 M.

(ii) If C is positive, hydroxide content = C; carbonate content = 2(P - C). No bicarbonate content. The total alkalinity M = C + 2(P - C) = 2P - C. P is more than 1/2 M.

(iii) If P = 1/2 M, the alkalinity is entirely due to carbonates, no hydroxides or bicarbonates being present.

(iv) If P = M, the alkalinity is entirely due to hydroxides, no carbonates or bicarbonates being present. P is also equal to C.

(v) If P = zero, the alkalinity is entirely due to bicarbonate, there being no carbonates or hydroxides in the water. Then M = bicarbonate content. C = zero.

4. CHLORIDE TEST

Purpose. In boiler-water conditioning the principal application of the chloride test is in the control of blow-down. Since chlorides are not subject to precipitation the determination of the relative chloride concentration of the feedwater and the boiler water provides the most accurate basis for calculating the rate of blow-down using the following formula:

$$\frac{\text{Cl in feedwater}}{\text{Cl in boiler water}} \times 100 = \% \text{ blow-down.}$$

Most waters contain only relatively small quantities of magnesium and calcium chlorides, both of which are hardness-producing salts which, under boiler conditions, promote scale formation and corrosion. Sodium chloride (common salt) is hardly existent in such water. In sea water, of course, sodium chloride is the major constituent of dissolved salts, approximately 25 620 ppm. The other chloride salt it contains is magnesium chloride, the quantity being about 3300 ppm. Of these, sodium chloride has a solubility of very nearly 224 000 ppm at ordinary temperatures and a much higher solubility under boiler conditions. Further, it does not undergo any chemical change in the boiler except under conditions of excessive temperature. In its dissolved condition, it is quite harmless, particularly with regard to scale formation or corrosion. Magnesium chloride, however, is an extremely undesirable constituent, since it promotes intensive corrosion and scale formation.

In the boilers of plants using estuarine water for cooling purposes, the presence of chlorides in the water can only mean that sea water is somehow finding its way into the plant. Sea-water leakage will result in a gradual concentration of dissolved sodium chloride. By itself, such concentration is not dangerous except when the solubility-saturation limit is reached and salt is deposited on the heating surfaces. But it is an indication that, together with sea water, other and more dangerous constituents such as magnesium chloride, calcium sulphate, etc., are introduced into the boiler. The measurement of chloride content is thus a sure method of ascertaining the existence of sea-water leakage into the feed system and the magnitude thereof.

Test. In the presence of potassium chromate in water, silver nitrate takes on a brick-red color owing to the formation of silver chromate. But silver nitrate has a greater chemical affinity towards sodium or other chlorides than for potassium chromate.

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Thus, when silver nitrate is added to a mildly acidic water (this is essential for promoting active chemical reaction) containing chloride salts as well as potassium chromate, a color change indicating formation of silver chromate takes place only when all the chloride salts have been reacted upon. This phenomenon is utilized in the measurement of dissolved chlorides in boiler water.

100 mL of filtered boiler water is taken in a porcelain dish and the alkalinity neutralized by the addition of N/50 sulphuric acid in sufficient quantity to remove the pink color caused by 10 drops of phenolphthalein. Excess acid up to 0.5 mL is then added making the sample under test distinctly acidic. 20 drops of potassium chromate is added to the sample, which is then titrated with N/50 standard silver nitrate solution. As each drop of silver nitrate strikes the sample, red color will appear momentarily but disappear immediately, as the chemical reactions between silver nitrate and the chlorides take place. The titration is continued till, with slight excess of silver nitrate, the sample acquires a reddish brown tinge (coffee color). The sample must be kept stirred throughout the process. The mL of silver nitrate added is recorded.

Calculation. Each mL of N/50 silver nitrate used neutralizes 10 ppm of chloride expressed in $CaCO_3$ ppm. Hence, chloride content in ppm of $CaCO_3$ = 10 times mL of silver nitrate added.

Chloride content can also be expressed in chloride ppm

35.5 Cl ppm = 50 $CaCO_3$ ppm

Therefore chloride content in terms of chlorine = $\frac{35.5}{50}$ x $CaCO_3$ ppm.

5. SODIUM SULPHITE TEST

Purpose. Feedwater carries with it into the boiler considerable quantities of dissolved oxygen, particularly in open-feed systems. This oxygen is freed out of solution when in the boiler and promotes corrosion of the boiler metal. This corrosive action of oxygen is particularly severe in high-pressure boilers. Efficient boiler management, therefore, requires that oxygen entry is reduced to the minimum and that the residual oxygen still finding its way in is immobilized through chemical treatment. The use of closed feed systems, de-aeration equipment, etc., assist in reducing the oxygen entering the boiler. Crystalline sodium sulphite has an affinity for oxygen and when combined with it becomes sodium sulphate. This chemical is, therefore, employed to neutralize the dissolved oxygen in the boiler water.

The formation of sodium sulphate is not an unmixed blessing. It increases the acid-forming solids in the water, which, in turn, call for increased addition of alkalis to counteract their effects. This results in increased scale and sludge formation and consequent reduction in boiler efficiency. Hence, this method of oxygen control is to be employed with overall consideration and only to keep the dissolved oxygen content down to a minimum value and not to eliminate it altogether. Keeping this in mind, only a very slight excess sodium sulphite is maintained (usually 20 ppm in the boiler water). The test is designed to measure this excess of sodium sulphite in the water.

Test. If a small quantity of starch solution is added to pure water and then the solution is titrated with potassium-iodide-iodate solution, a blue color is obtained instantaneously. In the presence of sodium sulphite, the reaction between potassium-iodide-iodate and the sodium sulphite takes precedence over the reaction between the former and the starch. So, the blue color is not formed until all the sodium sulphite has been chemically reacted upon by the potassium-iodide-iodate. This phenomenon of differing reactions of potassium-iodide-iodate in the presence or absence of sodium sulphite is utilized to test for excess sodium sulphite in boiler water.

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100 mL of boiler water is taken in a porcelain dish and is turned slightly acidic with the addition of N/50 sulphuric acid (so that chemical reactions may be accelerated). 1 mL of starch solution is then added and the solution then titrated with potassium-iodide-iodate solution until a permanent faint-blue color is obtained, the sample being kept stirred throughout. The mL of potassium-iodide-iodate solution used is recorded.

NOTE: It is of the utmost importance for the accuracy of the measurement that the sample should not be brought into contact with atmosphere, as the oxygen in air is bound to affect the sulphite content. Hence, the sample should preferably be drawn from the boiler through a cooling coil, the outlet end of which should reach the bottom of the measuring jar and the water allowed to overflow from the jar for a few minutes. This ensures an uncontaminated sample.

Calculation ppm sulphite as SO_3 = mL potassium-iodide-iodate x $\frac{500}{\text{mL sample}}$

Using a 100 mL sample the sulphite in ppm as SO_3 is equal to the mL of potassium-iodide-iodate required multiplied by 5.

6. PHOSPHATE TEST

Purpose. Modern boiler water conditioning is based on control of alkalinity and maintenance of zero hardness. With low-pressure boilers, the practice was to use soda ash (sodium carbonate) in order to control alkalinity. This alkali, however, is not very stable at high temperatures and pressures and breaks up into caustic soda (sodium hydroxide) and free carbon dioxide, resulting in caustic embrittlement of the boiler metal. Sodium phosphate compounds are milder alkalis, but more stable and very soluble in water at all temperatures and pressures in use. Hence, phosphate conditioning is the preferred treatment in high-pressure boilers.

There are three different phosphate compounds in popular use, viz. sodium metaphosphate, disodium-hydrogen-phosphate and trisodium phosphate. The alkalinity values differ between them. Hence the type of sodium phosphate compound used depends on the control of alkalinity. The main function of sodium phosphate in all cases is to precipitate the calcium salts in the feedwater as calcium phosphates and thus prevent formation of boiler scale. It is essential to ensure that there is, at all times, an excess of sodium phosphate in the boiler water.

Test. In the presence of sodium phosphate, a sample of boiler water with potassium nitrate crystals dissolved in it reacts to the addition of ammonium molybdate by becoming cloudy. The larger the quantity of sodium phosphate present, the quicker this reaction. The time taken for the onset of cloudiness is thus used as a measure of the excess phosphate in the boiler water.

50 mL of boiler-water sample, preferably hot, is taken in a flask and to it is added approximately 4 g of potassium nitrate crystals. The sample is then shaken for proper mixing and filtered several times till a clear sample is obtained. 25 mL of this filtered sample is then taken in a water bath and heated to a temperature between 38 and 40°C. 5 mL of filtered molybdate reagent is then added and the sample shaken thoroughly and allowed to stand for two minutes. A note is then made as to whether any cloudiness has set in. If the sample is still clear, an observation is again made after five minutes for the onset of cloudiness and the result recorded.

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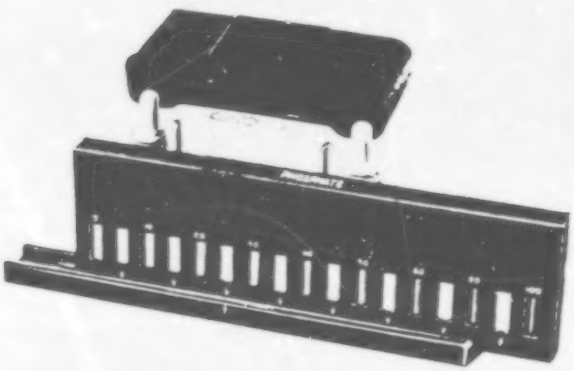
Interpretation. Onset of cloudiness of sample within two minutes indicates a phosphate reserve of more than 70 ppm.

Onset of cloudiness after two minutes but before five minutes indicates a phosphate reserve of between 20 and 70 ppm.

A clear sample even after five minutes indicates that the boiler water has less than 20 ppm of phosphate reserve.

The amount of excess phosphate is determined on the basis of the above rules of interpretation. It is generally desirable to maintain a soluble phosphate content of 30 to 60 ppm.

Alternative Test (Colorimetric method). This test is based on the production of a blue coloration through the use of molybdate and stannous reagents. The intensity of the colour produced being proportional to the amount of phosphate present.



Taylor Phosphate Comparator
Fig. 1

Fig. 1 shows a Taylor Phosphate Comparator used for this purpose. A filtered water sample treated with reagents in the centre test tube is color-matched with standard color windows in the slide. When a match is obtained the phosphate in parts per million as PO_4 is then read directly from the values on the color standard slide.

7. pH VALUE TEST

Introduction. Corrosion, in its general sense, is the process which results in metals being eaten away on the surface due to the formation of metal compounds such as oxides, chlorides, sulphates, etc. In recent years, this has formed the subject of serious scientific study and research, and a number of plausible theories have been put forward explaining the phenomenon of corrosion.

Principally, corrosion is regarded as an electro-chemical process which takes place when a metal is in contact with an electrolyte and two dissimilar galvanic elements are present in the liquid. It is, in fact, a chemical action between the metal itself on the one hand and the dissolved salts on the other. This chemical action is accelerated by the flow of electric current which is set up internally and externally between the two galvanic elements. Two basic conditions must be fulfilled in order to set up this electro-chemical action, namely,

(a) the presence of two galvanic elements at different electric potentials;
(b) the ability of the electrolyte to split into "ions" which serv e as vehicles for the flow of electric current through the liquid.

It is not absolutely necessary that the two galvanic elements be composed of two different metals. Even non-homogeneity of structure in the same metal may provide the necessary difference in electric potential to set up a flow of electric current through the circuit.

The second condition is fulfilled more fully if the electrolyte is "acidic", than if it is "neutral" or "alkaline". Thus corrosion is intensive in a boiler when the water inside is acidic. To ensure that this is prevented it is of benefit to keep the boiler water slightly alkaline at all times and thus counteract the formation of acids during the operation of the boiler.

The usual litmus paper test merely determines whether the water is markedly "acidic" or markedly "alkaline" but does not give a measurement of the degree of such acidity or alkalinity. An exact and sensitive measurement of acidity or alkalinity can be made on the basis of the ionic theory.

Ionic Theory. A normal atom is composed of a heavy nucleus which has a positive charge and of one or more electrons (with practically no mass) which circle around it. These electrons together have a negative electric charge which is equal but opposite to the positive charge of the nucleus. The two charges cancel each other out and the atom as a whole is neutral.

Under certain conditions, an atom attracts to itself an extra electron or loses, out of its own quota, an electron. This upsets the equilibrium and imparts to the atom as a whole a negative charge or a positive charge. A very similar process can happen to groups of atoms. An atom or a group of atoms which has a smaller or greater number of electrons than the normal complement is known as an ion. An ion will thus necessarily have a negative or positive electrical charge; and when two galvanic elements of different electric potential are present, it will move towards one of them.

In electrolysis, all liquids containing water show a tendency for a part of the water molecules to separate out into two kinds of ions, namely "hydrogen ions" and "hydroxyl ions". Hydrogen ions each have an electron short of normal complement and are, therefore, positively charged. Hydroxyl ions, on the other hand, each have an electron in excess and in consequence are negatively charged. When the number of hydrogen ions are exactly equal to the number of hydroxyl ions, the solution is said to be neutral. When the hydrogen ions are in greater number than the hydroxyl ions, the solution is an "acid". If the reverse is the case, it is an "alkali". In fact, it is the disparity in the numbers of the two types of ions that imparts to acids and alkalis their distinguishing qualities.

Pure water dissociates slightly into hydrogen and hydroxyl ions of equal number, but leaves the water as a whole neutral. There is very nearly one gram of hydrogen ions in each ten million litres of water. An equal number of hydroxyl ions is present. Since a single hydroxyl ions has a mass seventeen times that of a hydrogen ion, it follows that the mass of hydroxyl ions in each ten million litres of water is seventeen grams. Since 1 g-mass of hydrogen ions and 17 g-mass of hydroxyl ions represent the same number of ions, the quantities in both cases are defined as being "one gram-ion". This definition is very similar to the practice adopted in the definition of "gram-molecular mass" or "pound-molecular mass", when dealing with laws of gases. Thus, in 1 L of pure water, there are 10^{-7} g-ions of hydrogen ions and 10^{-7} g-ions of hydroxyl ions.

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By the law of mass action in chemistry, the product of concentrations of these hydrogen and hydroxyl ions is a constant for all solutions containing water. Thus, the product of 10^{-14} gram-ions per litre is constant. The addition of an acid substance like HCl (hydrochloric acid) or H_2SO_4 (sulphuric acid) increases the number of free hydrogen ions and to the extent this increase takes place, the number of hydroxyl ions is reduced so that the product of the two concentrations is constant at 10^{-14}.

Conversely the addition of an alkali substance like NaOH (caustic soda) increases the number of free hydroxyl ions and reduces the number of free hydrogen ions, again keeping the product of the two concentrations constant at 10^{-14}. This means that if in a water solution in which the hydrogen ion concentration is 10^{-7}, it is understood that it is neutral. If it is greater than 10^{-7}, say 10^{-5}, then it is acid. If it is smaller, say 10^{-9}, then it is alkaline. The expression "hydrogen ion concentration" is shortened by the term "pH value".

The pH Notation. Whatever the concentration of hydrogen ions in a particular sample of water solution, it can be represented in terms of a power of 10. The index alone will then be a variable quantity, and will invariably be a negative quantity. In order, however, to avoid the use of cumbersome exponential functions to express very small concentrations, the logarithm of the hydrogen ion concentration to the base 10, with sign reversed, is used for expressing acidity or alkalinity. Thus, a hydrogen ion concentration of 10^{-7} is expressed as "pH 7", that is, a neutral solution. Similarly, a hydrogen ion concentration of 10^{-9} is written as "pH 9", that is, an alkaline solution.

Thus, the determination of the pH value of a sample of boiler water gives a very accurate and clear picture of the condition of the water inside the boiler. In order to keep the water slightly alkaline, the pH value should always read more than 7.

There are two laboratory tests available for the measurement of pH values:

(i) Colorimetric measurement,
(ii) Electrometric measurement by battery-operated pH meter.

(i) Colorimetric Measurement of pH Values. The colorimetric method of the determination of pH value depends on the use of indicator solutions, the range of each solution being such that, arranged in ascending order, they cover a low pH value, say 4, to a high pH value, say 13. The treatment of the given boiler-water sample with these indicator solutions and the observation and comparison of the resulting color changes with the known properties of the indicators are the basic features of this method.

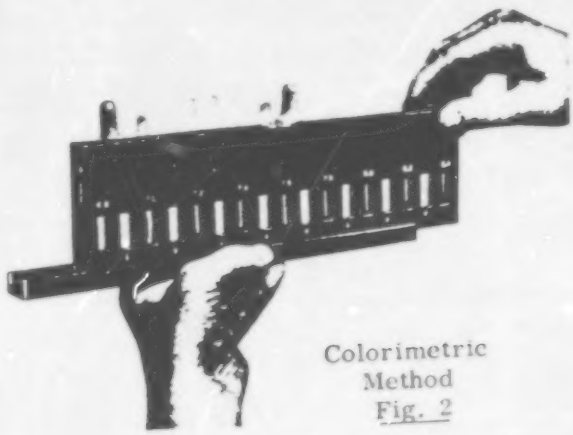
Table 2 gives the relevant particulars relating to a set of indicator solutions which are in use in laboratories for this purpose.

Fig. 2 illustrates the equipment.

TABLE 2 INDICATOR SOLUTIONS FOR pH VALUE DETERMINATION

Indicator	Original color of indicator	pH range in which color changes	COLOR	
			Below lower pH value	Above higher pH value
Brom cresol green	Green	4·0 - 5·6	Yellow	Blue
Chlorphenol red	Red	5·2 - 6·8	Yellow	Red
Phenol red	Red	6·8 - 8·4	Yellow	Red
Thymol blue	Blue	8·0 - 9·6	Yellow	Red
Thymolphthalein	Colourless	9·3 - 10·5	Colourless	Blue
Nitro yellow	Yellow	10·5 - 11·6	Yellow	Orange
Sulpho orange	Orange	11·0 - 12·6	Yellow	Orange

Test. Six test tubes are each filled with 10 mL of the boiler-water sample. A seventh tube is then filled with 10 mL of distilled water. To each of the six tubes with the sample under test, 0.5 mL of one of the six separate indicator solutions is added, at the same time taking care to ensure that no test tube receives more than one indicator solution. The indicator solutions are all graded in such a way that each of them indicates a definite range of pH value and that, between them, the range covered is between pH4 and pH12. The test tube which shows a change in color of the indicator solution is then noted and the pH range of the sample thus located.



Colorimetric Method
Fig. 2

This test tube is then placed in a pH comparator which is an instrument designed to determine the correct pH value of a sample, the pH range of which is already known. The correct pH value of the sample is thus determined and recorded.

The value obtained in this way is verified with the reading obtained from an electronic pH meter, if such an instrument is available.

(ii) Battery-operated pH meter. In this method of evaluation of pH value, a special type of cell consisting of a glass and a calomel electrode is used, the boiler water sample under test being used as the electrolyte. The potential between these two electrodes varies directly with the amount of hydrogen ion concentration in the solution. Hence the measurement of this potential by means of a voltmeter will give the pH value if the calibration of the instrument is in pH numbers instead of volts.

However, with the use of a plain voltmeter directly across the two electrode terminals, accurate measurement of the electrode potential becomes difficult. Hence an adjustable external voltage is utilized to balance this electrode potential and the pH value is directly read on a highly sensitive voltmeter. This is the principle underlying the pH meter, although for purposes of sensitive measurement and elimination of possible errors from all sources, a complicated electronic instrument of great sensitivity is employed.

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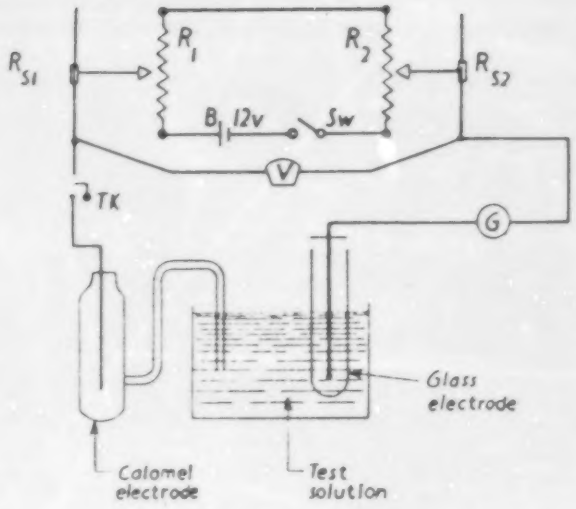
In reality, the pH meter is a voltmeter with its scale calibrated to read the pH value. Fig. 3 brings out clearly the principle of operation of the pH meter.

Referring to the figure: R_1, R_2 = resistances; R_{S1}, R_{S2} = adjustable resistances; B = dry battery; Sw = switch; TK = tapping key; G = Galvanometer; V = voltmeter calibrated to read pH value directly.

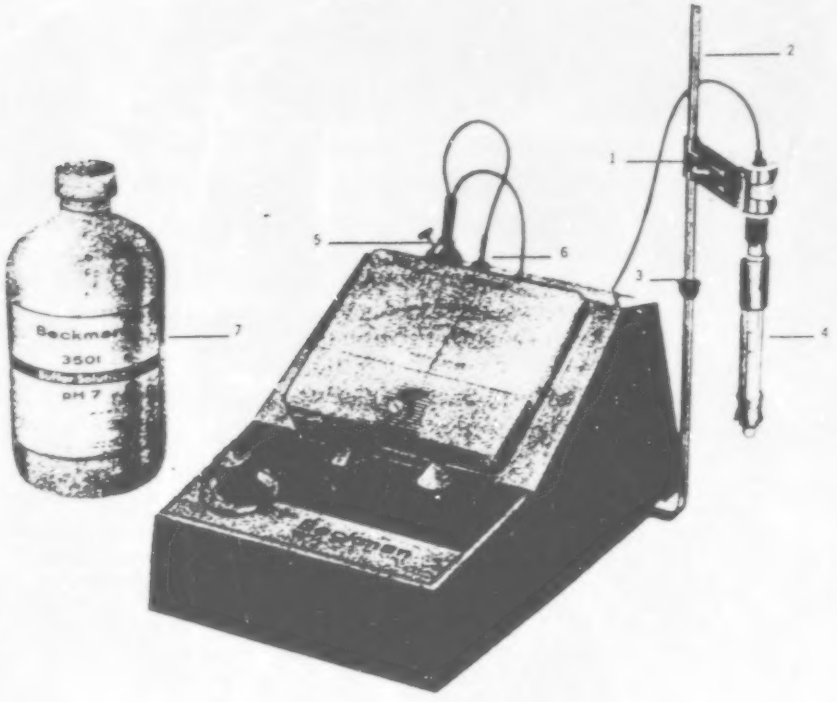
Tabulation of Results

The results of the various tests should be entered in a tabulated analysis report for purposes of record. To ensure that the results are free from errors, it is recommended that every test be conducted three times and the mean value of the three tests accepted as correct.



Principle of Operation of the pH Meter
Fig. 3

Fig. 4 shows a Beckman model 72 pH meter assembly.



1. Electrode Clip
2. Support Rod
3. Electrode Stop
4. Combination Electrode
5. Glass Electrode Terminal
6. Reference Electrode Terminal
7. Buffer Solution

Beckman Model 72 pH meter Assembly
Fig. 4

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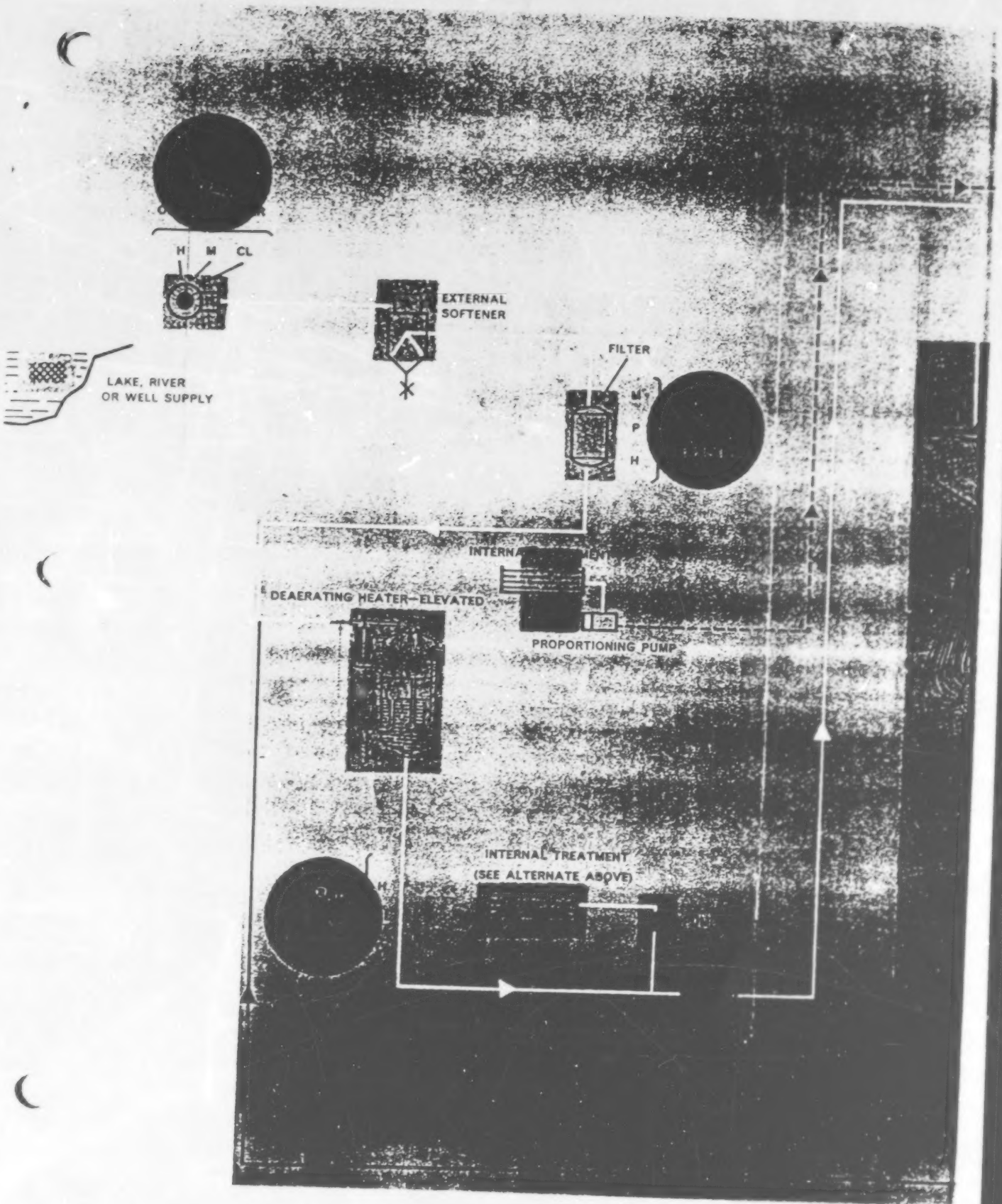

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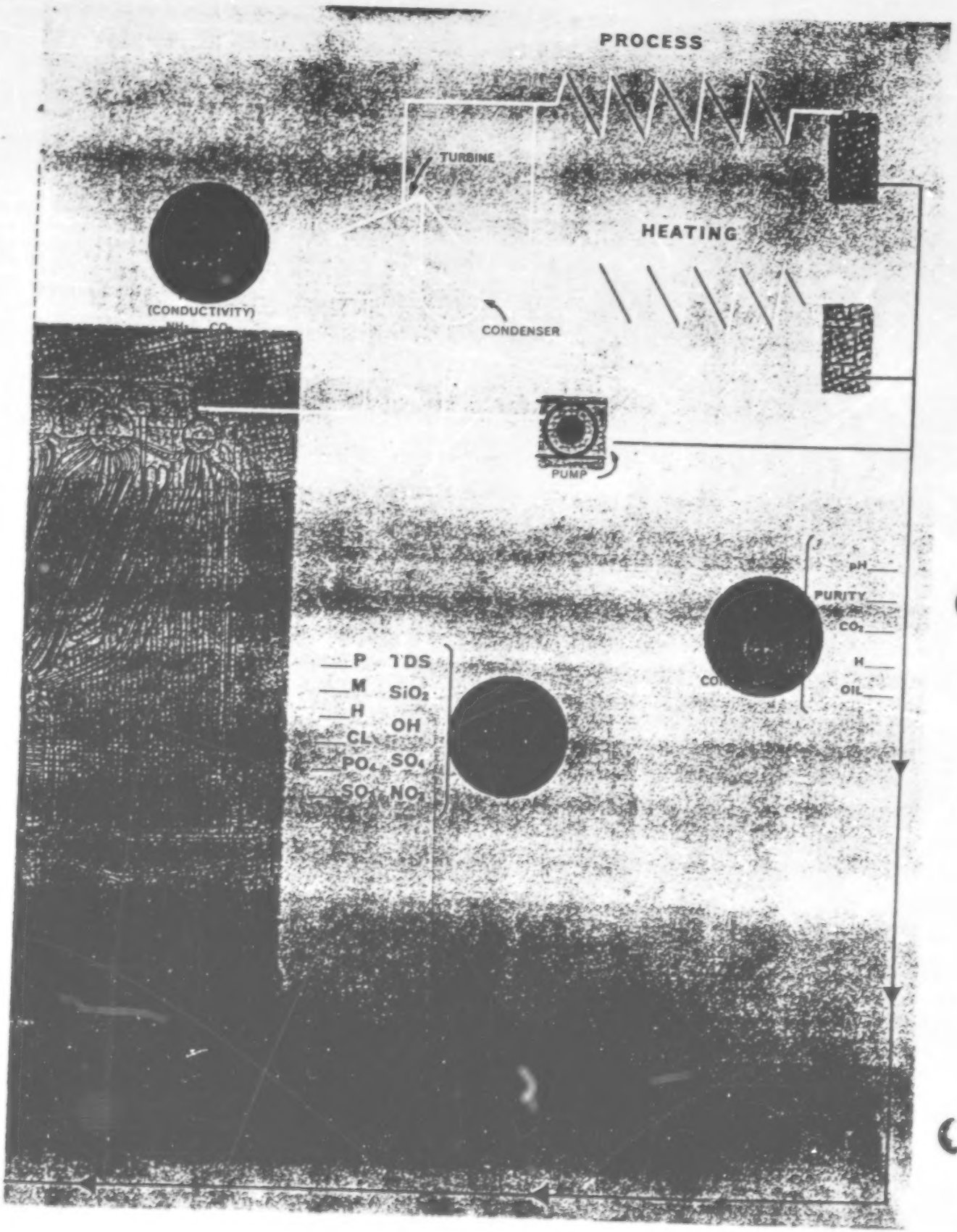

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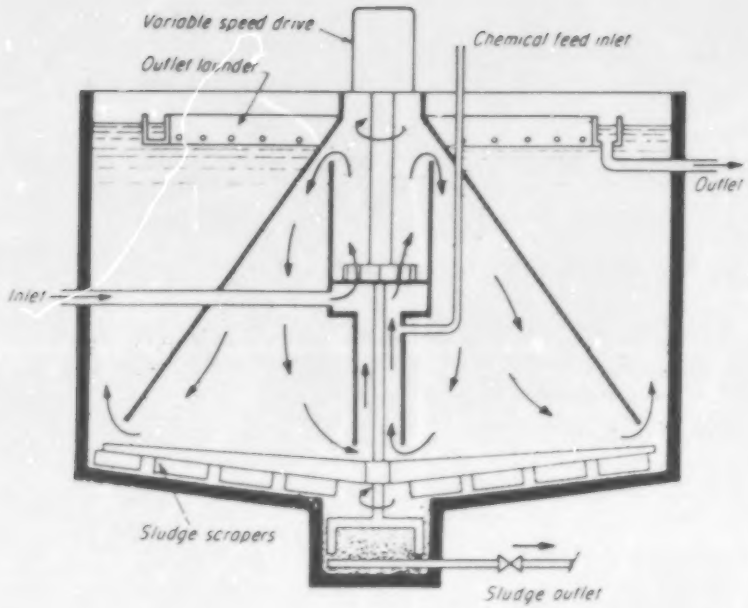
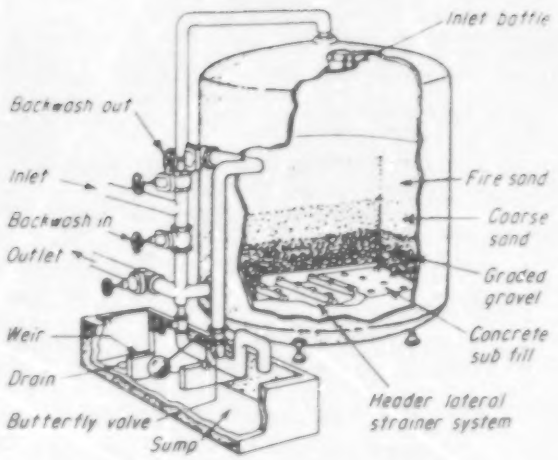


Clarifier
Fig. 6

Filter rates are usually between 100 to 200 $L/m^2/min$ of filter area and may be built in sizes of 0.3 to 3 m in diameter, and 1.25 to 1.5 m in height.

Filters are kept in effective condition by backwashing; pressure-head drop across the bed will indicate the progress of fouling. The backwash rate must be controlled so as to effectively clean the filter medium but not cause vilent agitation of the bed and losses of filter material. An average figure might be 75 L/m^2 min.

Usually these filters will be installed in parallel so that one at a time may be closed off from the water flow and backwashed.



Filter
Fig. 7

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Lime-Soda Softening

Lime-soda softening is employed for the removal of hardness in order to minimize scale and sludge; incidental to this removal of hardness, free carbon-dioxide will be removed and turbidity reduced.

The process may be carried out Cold or Hot. Addition of heat speeds the completion of the reactions. The Hot process is usually employed in boiler water treatment, using as a heat source either live or exhaust steam.

Figs. 9 and 10 give diagrams of common types.

Chemical Processes

Hydrated lime, $Ca(OH)_2$, produced from unslaked lime, (CaO), and water is used to chemically precipitate the carbonate (temporary) hardness in water as follows:

(1) $Ca(HCO_3)_2$ + $Ca(OH)_2$ = $2CaCO_3$ + $2H_2O$

Calcium Bicarbonate + Calcium Hydroxide = Calcium Carbonate + Water

and

(2) $Mg(HCO_3)_2$ + $2Ca(OH)_2$ = $Mg(OH)_2$ + $2CaCO_3 + 2H_2O$

Magnesium Bicarbonate + Calcium Hydroxide = Magnesium Hydroxide + Calcium Carbonate + Water

The hydrated lime also reacts to precipitate the sulphate and chloride (permanent) hardness in accordance with the following:

(3) $MgSO_4$ + $Ca(OH)_2$ = $Mg(OH)_2$ + $CaSO_4$

Magnesium Sulphate + Calcium Hydroxide = Magnesium Hydroxide + Calcium Sulphate

and

(4) $MgCl_2$ + $Ca(OH)_2$ = $Mg(OH)_2$ + $CaCl_2$

Magnesium Chloride + Calcium Hydroxide = Magnesium Hydroxide + Calcium Chloride

The Calcium sulphate and Calcium Chloride resulting from these reactions together with that naturally present in the water then reacts with the soda ash (Sodium Carbonate) as follows:

(5) $CaSO_4$ + Na_2CO_3 = $CaCO_3$ + Na_2SO_4

Calcium Sulphate + Sodium Carbonate = Calcium Carbonate + Sodium Sulphate

and

(6) $CaCl_2$ + Na_2CO_3 = $CaCO_3$ + 2NaCl

Calcium Chloride + Sodium Carbonate = Calcium Carbonate + Sodium Chloride

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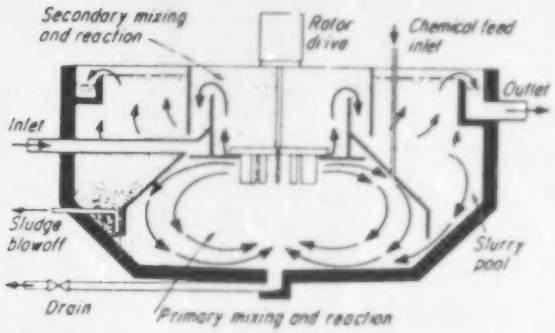
It will be seen from the above reactions that conversions have been made from calcium and magnesium sulphates to calcium carbonate and magnesium hydroxide.

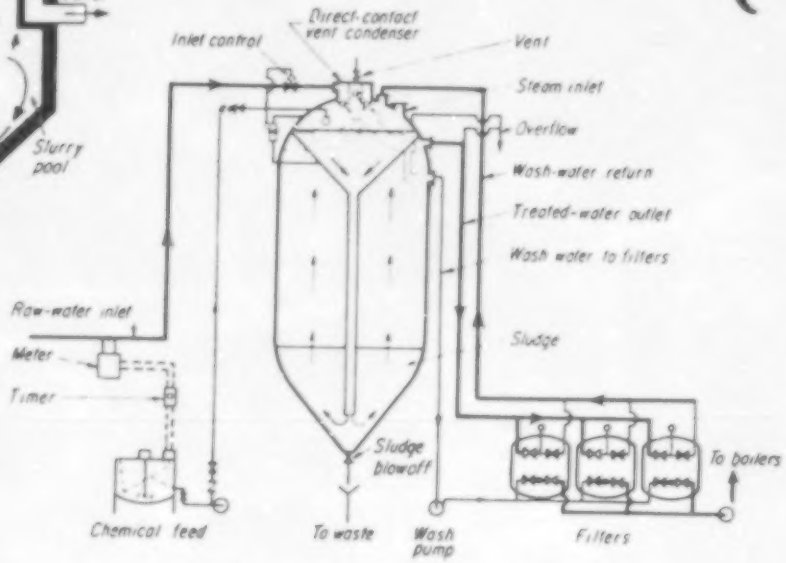
These conversions are aimed firstly at complete precipitation of all of the calcium and magnesium salts and secondly, in the event that some salts do enter the boiler, that they should be calcium carbonate rather than calcium sulphate, and magnesium hydroxide rather than magnesium sulphate.

Boiler scales are generally made up of a mixture of substances - depending upon boiler conditions and vary considerably in hardness and texture. Chemical analysis has shown that the chief constituents of hard scales are calcium sulphate and calcium and magnesium silicates. On the other hand soft sludges are composed mainly of calcium carbonate and magnesium hydroxide.

Calcium sulphate in particular is the main scale forming constituent found in boiler water and when thrown out of solution on a hot metal surface, forms a hard dense scale which adheres tenaciously.



Cold Lime Soda Softener
(Sludge-contact type)
Fig. 9



Hot Lime Soda Softener
(Deaerating type)
Fig. 10

Hot Process Phosphate Softening

Hot phosphate softening is employed in the treatment of feedwaters which are low in hardness and alkalinity but high in turbidity. It may be used as a follow-up process to hot lime soda softening, though the development of ion exchange resins has made ion exchange softening more advantageous.

Silica reduction is accomplished in the hot phosphate softener by magnesium sulphate.

In addition, phosphoric acid and/or sulphuric acid may be used prior to softening in order to reduce alkalinity and assure a low carbon dioxide content in the steam.

Sodium Zeolite Softening

Impurities that dissolve in water dissociate to form positively and negatively charged particles known as ions.

The positive ions are named cations because they migrate to the negative electrode (cathode) in an electrolytic cell. Negative particles are then anions since they are attracted to the anode. These ions exist throughout the solution and act almost independently. For example, magnesium sulphate ($MgSO_4$) dissociates in solution to form positive magnesium ions and negative sulphate ions. Generally all natural waters contain electrolytes in varying concentrations.

Ion exchange material has the ability to exchange one ion for another, hold it temporarily in chemical combination and give it up to a strong regenerating solution. All ion exchange materials are commonly called Zeolites though they are divided into anion exchangers and cation exchangers.

Sodium Zeolite softening is by far the most common of the exchange reactions involved in water conditioning and is generally the one referred to when the term "Zeolite softening" is used without further qualification.

Ion exchange (as mentioned above) is divided into two groups.

(a) Cation exchangers (operating either on the sodium cycle or the hydrogen cycle) such as natural greensand, syntactic gel, sulphurated coal, styrene resin.

(b) Anion exchangers (either weakly basic or strongly basic), aliphatic amine, phenolic.

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Those materials operating on the sodium cycle, as used in Sodium Zeolite softening, regardless of how they have been produced, have a complex molecule with sodium attached. They are represented in a chemical equation by using the symbol Na_2 where Na stands for the sodium and Z for the complex zeolite radical so that the reaction in sodium zeolite softening is as follows:

Ca^{++}	+	Na_2Z	=	CaZ	+	Na_2
Calcium		Sodium		Calcium		Sodium
Ion	+	Zeolite		Zeolite	+	Ion

When this reaction has proceeded to the point where the zeolite will release no more sodium in exchange for calcium it becomes necessary to regenerate the zeolite bed.

Regeneration is accomplished by washing with a strong salt solution (sodium chloride). The high concentration of the sodium ion in the salt solution reverses the reaction as follows:

CaZ	+	2NaCl		Na_2Z	+	$CaCl_2$
Calcium		Sodium		Sodium		Calcium
Zeolite	+	Chloride	=	Zeolite	+	Chloride

The calcium placed in solution by this regeneration is run to waste as calcium chloride.

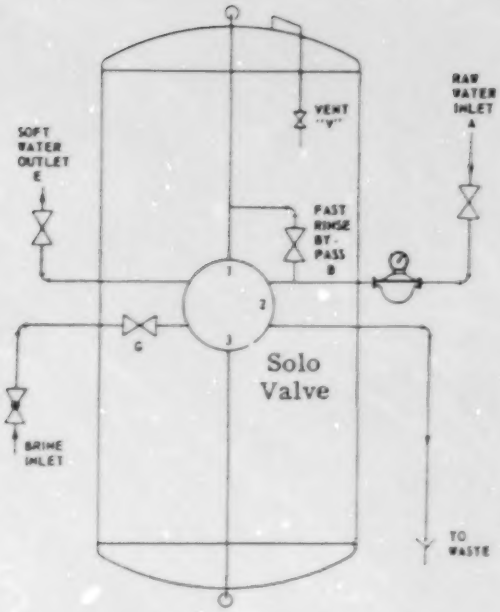
Fig. 11 shows Regenerating Instructions and diagrams of a Bird Archer Solo Valve.

Fig. 12 shows the "Cochrane" Zeolite Softener.

Sodium zeolite softeners require very little maintenance and are simple to operate. They are <u>not</u> suitable however, for all water, e.g. turbid water coat the zeolite grains and reduce efficiency, in this case filtration preceded by coagulation is necessary and consequently lime soda softening may be preferable.

One of the principal disadvantages of sodium zeolite softening is that the hardness is removed without a reduction in alkalinity or total solids. If the natural alkalinity of the water is not low in comparison with total solids, sodium zeolite softening results in high boiler-water alkalinity and high carbon dioxide concentration in the steam. This condition often requires high rates of blowdown to maintain reasonable boiler water alkalinities. High alkalinities are objectionable as they tend to promote both carry-over and caustic metal embrittlement (intercrystal line cracking).

REGENERATING INSTRUCTIONS



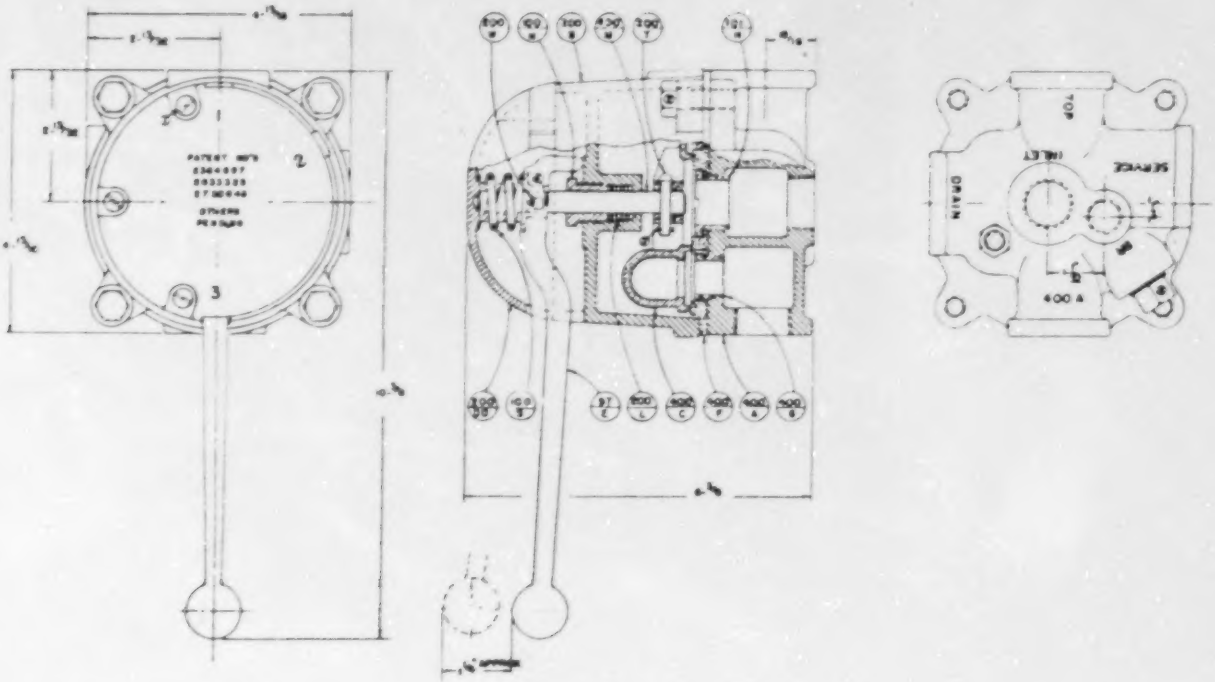
Backwash: Close valves "A" and "E". Rotate Solo Valve to position 1. Slowly open valve "A". If large zeolite particles wash to drain, throttle "A". Wash until effluent is clear but not less than time given at right . .

Inject: Close valve "A". Rotate Solo Valve to position 2. Open valves "A" and "G". Rate cock on brine inlet should be set for correct flow.

Displace: Close valve "G". Solo Valve remains in position 2. Allow water to flow to waste.

Rinse: Open valve "B". Solo Valve remains in position 2. Fast rinse to sump at rate of . . . . . or until hardness is reduced sufficiently to return unit to service. Close valves "A" and "B".

Service: Rotate Solo Valve to position 3. Reset meter dial for desired gallonage per regeneration. Open valves "A" and "E". Open vent valve "V" frequently during service run. Check hardness at regular intervals.



(PE2-2-7-26) Typical Regeneration Diagram and Instructions
Fig. 11

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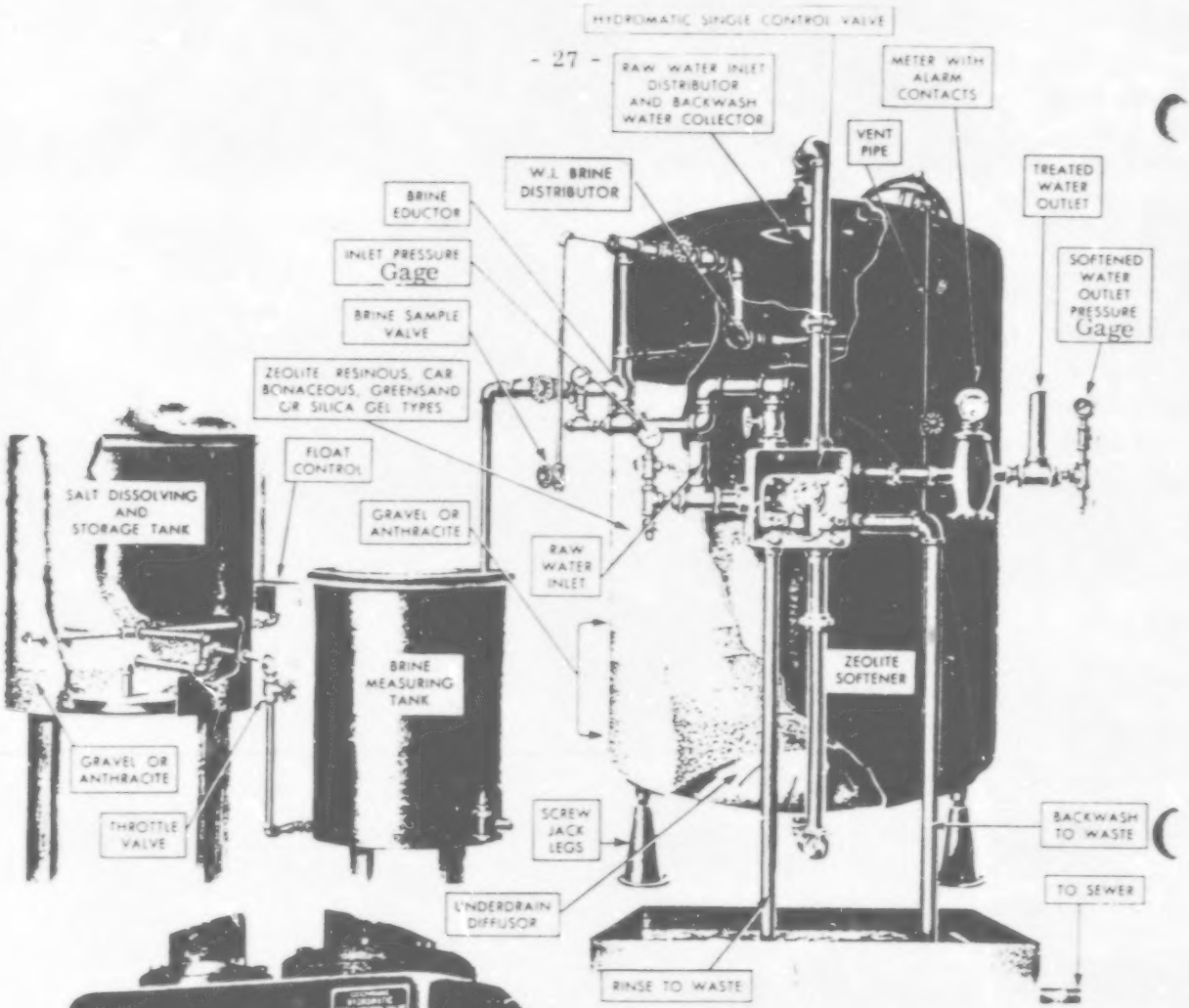
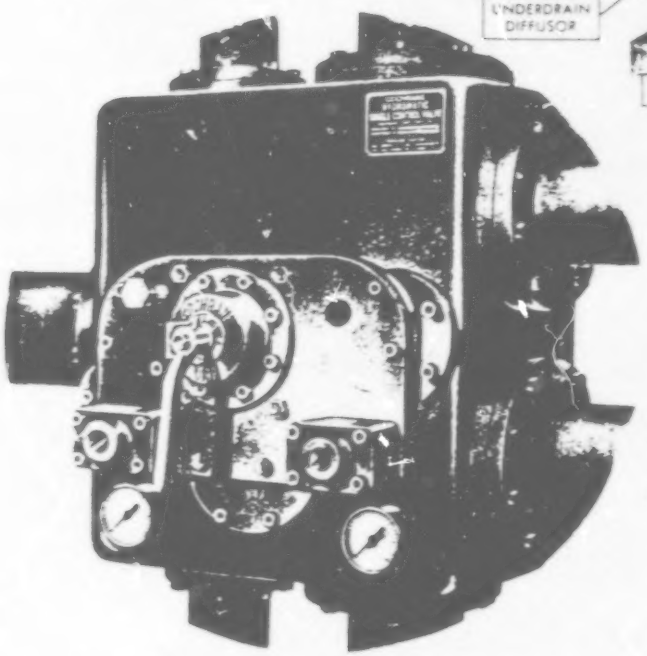




Enlarged view of
Cochrane Hydromatic Valve
(Manual Operation)

COCHRANE ZEOLITE SOFTENER

with

HYDROMATIC SINGLE CONTROL VALVE

and

DIFFUSOR UNDERDRAIN

Fig. 12

(PE2-2-7-27)

Hydrogen Zeolite Cation Exchange

Hydrogen zeolite is a material which has the ability to exchange hydrogen for the cations of calcium, magnesium, sodium etc. Regeneration of the hydrogen zeolite bed is carried out with acid; sulphuric acid is usually chosen because of its low cost.

When water containing calcium, magnesium and sodium ions is passed through a hydrogen zeolite, these ions are exchanged for hydrogen and the bicarbonate, sulphate, nitrate and chloride radicals are converted to their respective acids, namely, carbonic acid, (H_2CC_3), sulphuric acid,(H_2SO_4), nitric acid,(HNO_3), and hydrochloric acid, (HCl). When the zeolite becomes exhausted it is backwashed and regenerated with acid.

The carbonic acid (H_2CO_3) is very unstable in water and can easily be removed by aeration or degasification.

The other acids, sulphuric, nitric and hydrochloric must be neutralized to prevent acidic corrosion of the pipework etc. This can be done by using alkali such as caustic soda (NaOH) or soda ash (Na_2CO_3) but the cost of chemicals will be high if the quantity of water is great.

Alternatively the hydrogen zeolite softener may be combined with a sodium zeolite unit.

Fig. 13 shows hydrogen zeolite and sodium zeolite units in parallel followed by a degasifier, and Fig. 14 shows the layout using hydrogen zeolite followed by degasifier and alkaline neutralizer.

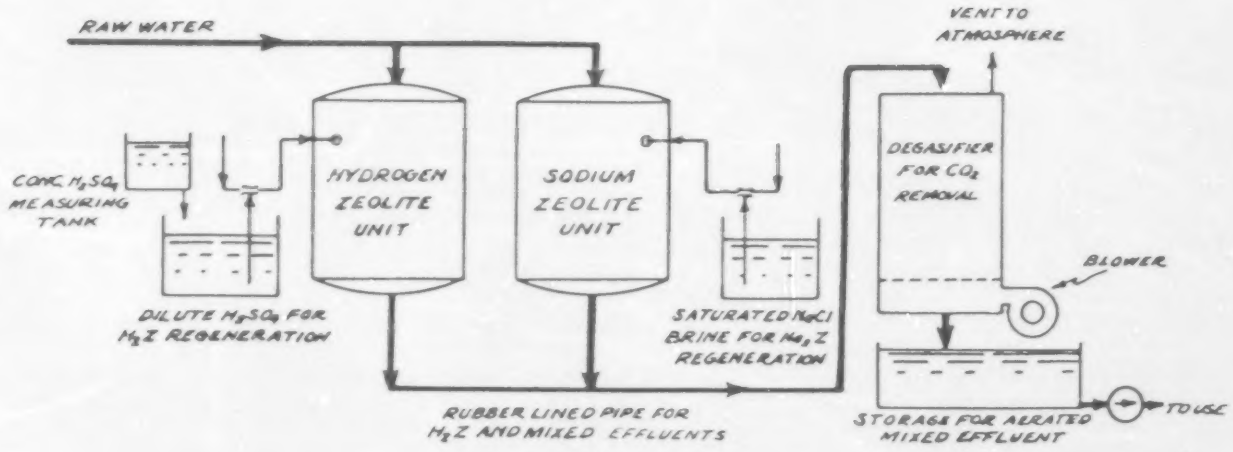
Note that the sodium zeolite unit is placed in parallel with the hydrogen unit, the quantity of water passing through the sodium unit must be carefully calculated so as to produce final treated water of the desired alkalinity.

Cation exchange methods of water softening by hydrogen zeolite as described above are used principally on water which is low in hardness but high in bicarbonate alkalinity.

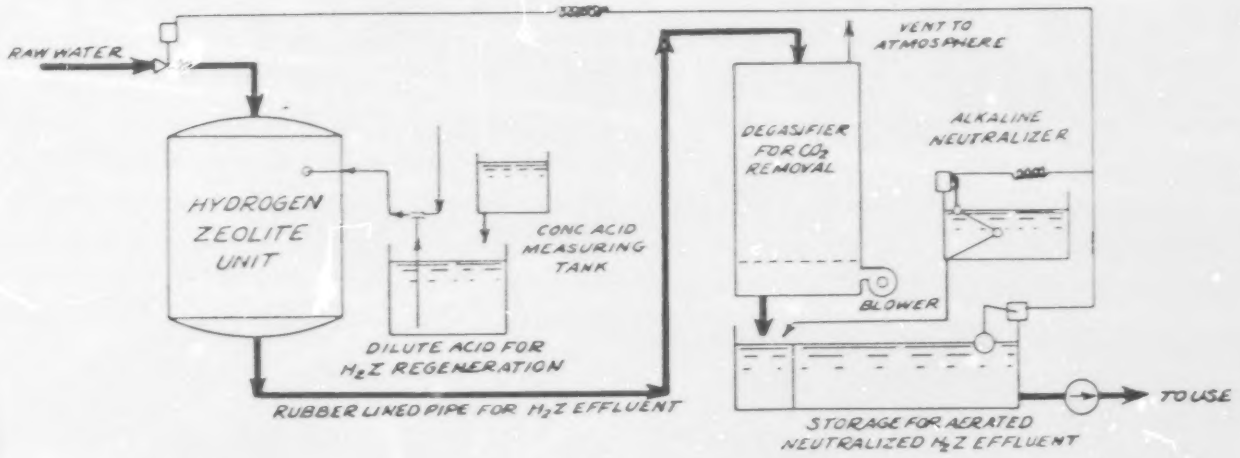
Demineralization

Demineralizing by ion exchange has proved an efficient means of removing dissolved salts from water. Treated water is produced that is the equivalent of distilled water, free of all except traces of salts, gases or silica.

Dissolved salts in water ionize (or split) into charged particles called ions, positive cations and negative anions.



Hydrogen and Sodium Zeolite units in Parallel
Fig. 13



Hydrogen Zeolite with Alkali Neutralization
Fig. 14

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The ion exchange process takes place in two steps, first the positive metallic ions (cations) calcium, magnesium, and sodium are removed by a cation exchange unit using hydrogen zeolite, and secondly the remaining negative ions (anions) sulphates, chlorides, etc. are removed by the anion exchanger. The acids produced in the first (cation) exchange process are also removed in the second (anion) exchanger process to complete the demineralization and produce a water of extreme purity.

Prior to the relatively recent development of the highly basic anion exchange resins, demineralization of a water by ion exchange did not lower the silica content. Without silica removal demineralization possessed limited application in the preparation of boiler feedwater since the silica would permit the formation of boiler scale or vaporize with the steam and cause turbine blade deposits.

Highly basic anion resins are capable of absorbing silica from demineralized water so that the process becomes as effective as evaporation (distillation) and is very frequently less costly.

The chemistry of demineralization is as follows:

Cation Exchange

CaA	+	H_2Z	=	CaZ	+	H_2A
MgA	+	H_2Z	=	MgZ	+	H_2A
Na_2A	+	H_2Z	=	Na_2Z	+	H_2A
Salts	+	Hydrogen Zeolite	=	Used Zeolite	+	Acids

The letter A represents the bicarbonate, sulphate or nitrate present in the water with calcium, magnesium and sodium. The letter Z represents the zeolite material. H_2Z represents a zeolite or cation exchange material in which the exchangeable ion is hydrogen. The salts in the water react with the exchange material and the cations (calcium, magnesium and sodium) remain with the used zeolite. Hydrogen replaces the other cations in the water forming dilute acids.

(PE2-2-7-30)

Hence the sulphates, chlorides and nitrates form free mineral acids (F.M.A.) as follows:

$MgSO_4$	+	H_2Z	=	MgZ	+	H_2SO_4
Magnesium Sulphate	+	Hydrogen Zeolite	=	Magnesium Zeolite	+	Sulphuric Acid
2NACl	+	H_2Z	=	Na_2Z	+	2HCl
Sodium Chloride	+	Hydrogen Zeolite	=	Sodium Zeolite	+	Hydrochloric Acid

Bicarbonate salts in the water form carbonic acid:

$Ca(HCO_3)_2$	+	H_2Z	=	CaZ	+	$2H_2CO_3$
Calcium Bicarbonate	+	Hydrogen Zeolite	=	Calcium Zeolite	+	Carbonic Acid

Carbonic acid will in turn form free CO_2 gas:

Carbonic Acid	=	Carbon Dioxide	+	Water

Anion Exchange

In the second stage, the anion exchanger has a mixed bed of both stronly basic and weakly basic anion exchange resins. Together they remove the remaining negative ions (anions) sulphates, chlorides, etc. and also the acids, carbon dioxide and silica:

H_2SO_4	+	$R(OH)_2$	=	RSO_4	+	$2H_2O$
Sulphuric Acid	+	Hydroxide Resin	=	Sulphate Resin	+	Water
2HCl	+	$R(OH)_2$	=	RCl_2	+	$2H_2O$
Hydrochloric Acid	+	Hydroxide Resin	=	Chloride Resin	+	Water
CO_2	+	$R(OH)_2$	=	RCO_3	+	H_2O
Carbon Dioxide	+	Hydroxide Resin	=	Carbonate Resin	+	Water
H_2SiO_3	+	$R(OH)_2$	=	$RSiO_3$	+	$2H_2O$
Silica	+	Hydroxide Resin	=	Silica Resin	+	Water

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Regeneration is carried out by first backwashing to clean the beds, and in the case of mixed beds, to classify the resins. (Here the lighter resin settles to the bottom. A sharp line of demarcation is visible through a sight glass on the side of the tank.)

Cation exchange units are regenerated with acid, usually N/50 sulphuric, and the anion exchange units are regenerated with caustic soda.

Degasification is included in the demineralizing process in order to remove the carbon dioxide gas which has been released in the process.

Fig. 15 shows the demineralization layout and Fig. 16 a degasifier.

Fig. 17 shows a block diagram prepared by Messrs. Graver showing the ppm of silica, hardness, alkalinity, sulphates and chlorides of a typical raw water and the quantities remaining after treatment by various methods.

Internal Water Conditioning

The methods of water treatment described in the preceding material are carried out before the water is supplied to the boilers, so-called water softening. A final adjustment to the water purity is almost always required however, and this is done by injecting chemicals directly into the boiler or its feed system, so-called conditioning.

The final conditioning of a boiler feedwater is the process whereby the metallic and acid radicals are so adjusted that only calcium or magnesium salts of positive solubility characteristics are produced. The chemicals used for this purpose are soda ash (Na_2CO_3) or sodium phosphate. The use of soda-ash is limited to temperatures of about 200°C (1750 kPa pressure) the reason being that above these temperatures sodium carbonate hydrolyses in solution producing NaOH and CO_2 gas which passes away with the steam. Sodium phosphate however is stable at all boiler operating temperatures so far encountered and does not decompose.

The phosphate used may be sodium, disodium, trisodium or sodium metaphosphate according to the water alkalinity. The usual practice is to inject these chemicals directly into the boiler drum on a continuous basis, using a small high-pressure ram pump for the purpose.

Chemicals used to control the oxygen content of the boiler water are sodium sulphite (Na_2SO_3) and hydrazine (N_2H_4). Use of sodium sulphite is usually restricted to boiler water temperatures below about 260°C (4900 kPa) because of a tendency for H_2S gas to be formed and carried off with the steam.

These chemicals are usually pumped continuously into the suction side of the boiler feed pump in order to give protection to the whole feed system.

In addition to the above mentioned chemicals, amines and colloids may be [illegible] protection against oxygen and carbon dioxide attack in the plant piping system and to assist in producing a fluid sludge in the boiler.

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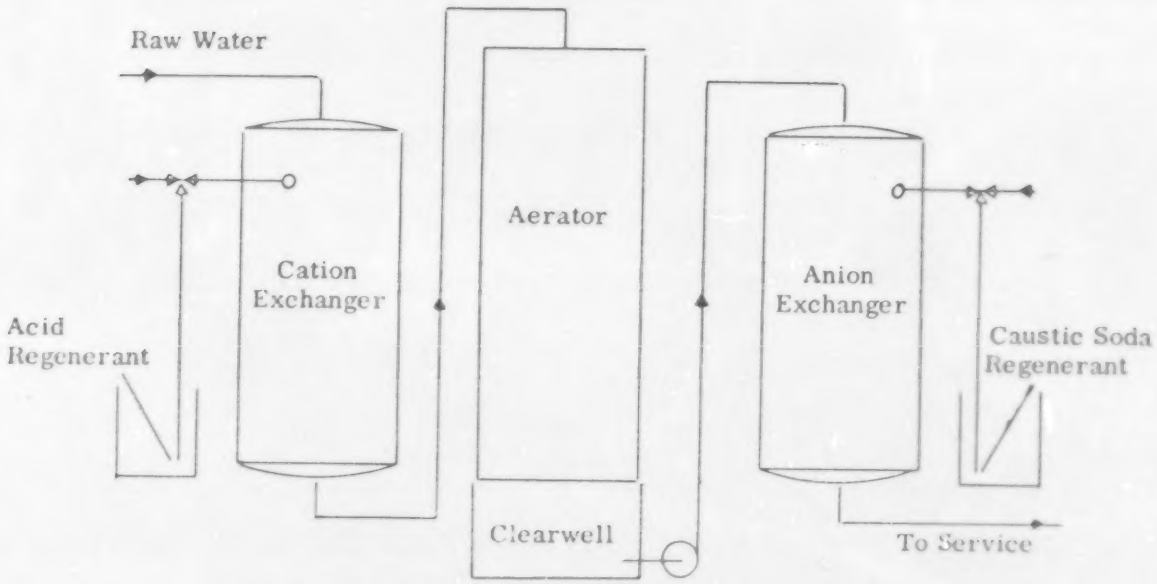
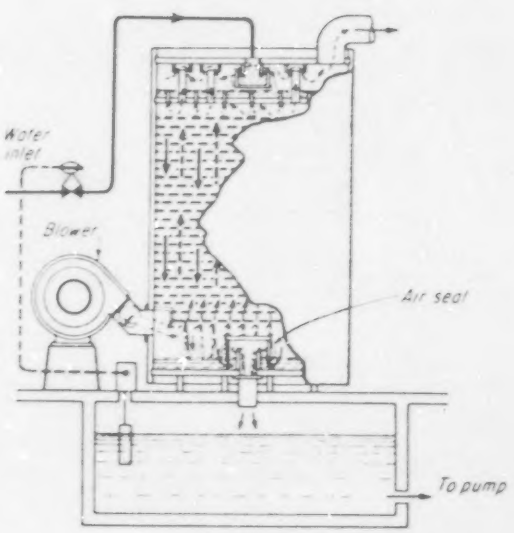
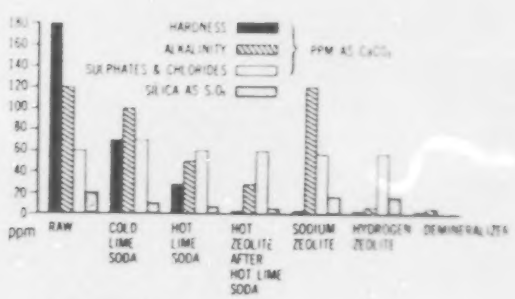


Two-bed System with Aerator for Demineralization and Silica Removal
Fig. 15



Degasifier
Fig. 16



Typical Water Impurity Quantities
Fig. 17

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Fig. 18 shows a typical proportioning pump used for injecting boiler chemicals. These pumps must be positive displacement in order to overcome the high pressure in the boiler and they must also be capable of accurate control of discharge quantity.

The pump shown is a reciprocating pump with an infinitely variable stroke. Rotation of the control knob and its threaded spindle sets the position of the slide on the piston drive rocker arm and consequently the length of the piston stroke.

Evaporation

Pure water can be produced by a process of distillation. This is done by boiling the raw water followed by condensation of the steam produced. All impurities are left behind except entrained gases; if these are given an opportunity to vent, the water produced is pure.

The process is expensive in terms of heat required and will only be used where it can be proved to be economically sound.

Evaporators are described in Lecture 9, Section 3.

Chemical Cleaning

Chemical cleaning of boilers and pressure vessels can be carried out by various means and is widely adopted because of the difficulty of access in modern high-pressure units for mechanical cleaning.

Off-load cleaning is carried out using inhibited acid (usually dilute hydrochloric) either by soaking or by circulating until reaction between acid and scale ceases.

These methods have the disadvantage of plant-outage time and recently some success has been achieved with on-load cleaning using chelating agents.

Chelating agents, in contrast to phosphates which precipitate scale-forming salts as sludge, function by forming complex soluble salts. This capacity is so predominant that materials which have already been precipitated can be solubilized under boiler operating conditions, thus existing deposits can be removed by the application of a suitably balanced program.

The basic chelating agents are the sodium salts of ethyldiaminetedra acetic acid and nitrilotriacetic acid.

Mechanical Deaeration is the term applied to the reduction of oxygen content of feedwater by means other than chemical treatment. Fig. 19 shows the volume of air, oxygen and carbon dioxide capable of remaining in solution in water at different temperatures and atmospheric pressure.

These gases can be dispelled if the water temperature is raised to boiling point and is the principle of mechanical deaeration. Feedwater heaters and deaerators are used for the purpose. This equipment will be described in Lecture 9, Section 3.

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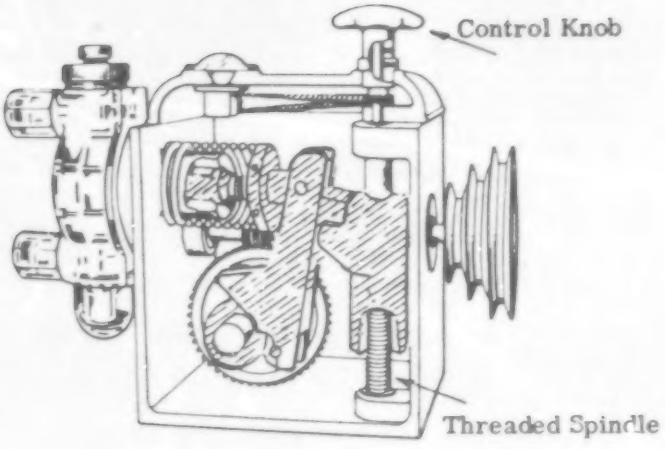
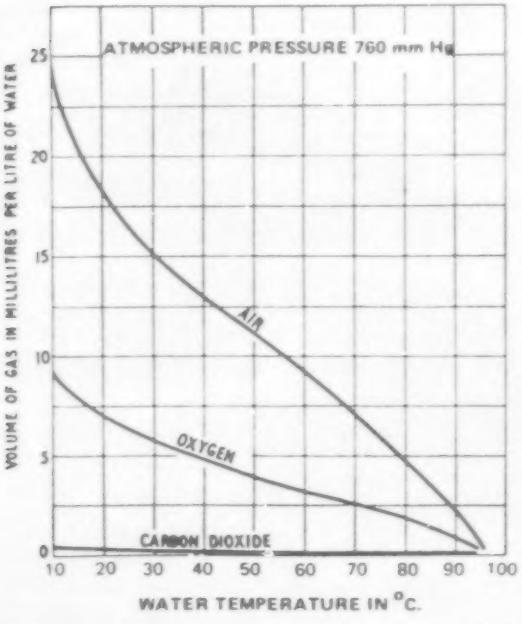


"Chem-O-Feeder" Mechanism
(Cut-away View)
Fig. 18



Volume of air, oxygen and carbon dioxide in water at different temperatures when saturated with air at atmospheric pressure
Fig. 19

(PE2-2-7-35)

QUESTION SHEET

POWER ENGINEERING

Second Class
Sect. 2, Lect. 7

1. State the aims of boiler water treatment, and define "water softening" and "water conditioning".

2. Draw up a schedule of water tests designed to ensure the correct operation of a steam power plant. Say:
   (a) what tests should be carried out,
   (b) why these have been chosen, and
   (c) where in the plant cycle the test samples should be taken.

3. (a) Define T.D.S.
   (b) Describe a method of test used and the apparatus employed to find the T.D.S. of a sample of boiler water.
   (c) What is a permissible level of T.D.S. in the water of a boiler operating at 4500 kPa?
   (d) How would you control this level?

4. (a) What is understood by "hardness" in a boiler water?
   (b) Distinguish between "temporary" and "permanent" hardness, and
   (c) State the effects of these on boiler heating surfaces.

5. (a) What are the main methods used to overcome boiler water hardness?
   (b) How would you decide which method to use in any particular case?

6. What are the purposes of the following water tests (give brief statements only):
   1. Alkalinity
   2. Chloride
   3. Sodium Sulphite, and
   4. Phosphate.

7. (a) What is meant by the pH value of a boiler water.
   (b) Explain carefully the derivation of the term.
   (c) Say what bearing the pH value has upon the action of the water upon the internal surfaces of the boiler.

8. Explain the following terms:
   1. Reagent
   2. Electrolysis
   3. Clarification
   4. Solubility
   5. Indicator
   6. Hydrogen ion Concentration
   7. Coagulation
   8. Titration
   9. Flocculation.

9. (a) What is meant by steam purity?
   (b) How is it measured, and
   (c) What would be considered as harmful contaminants.

10. Give a full description, with sketches and chemical reactions, of one of the main methods of water softening.